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Sulfide Precipitation of Heavy Metals

Boeing Commercial Airplane Co.
Seattle, WA

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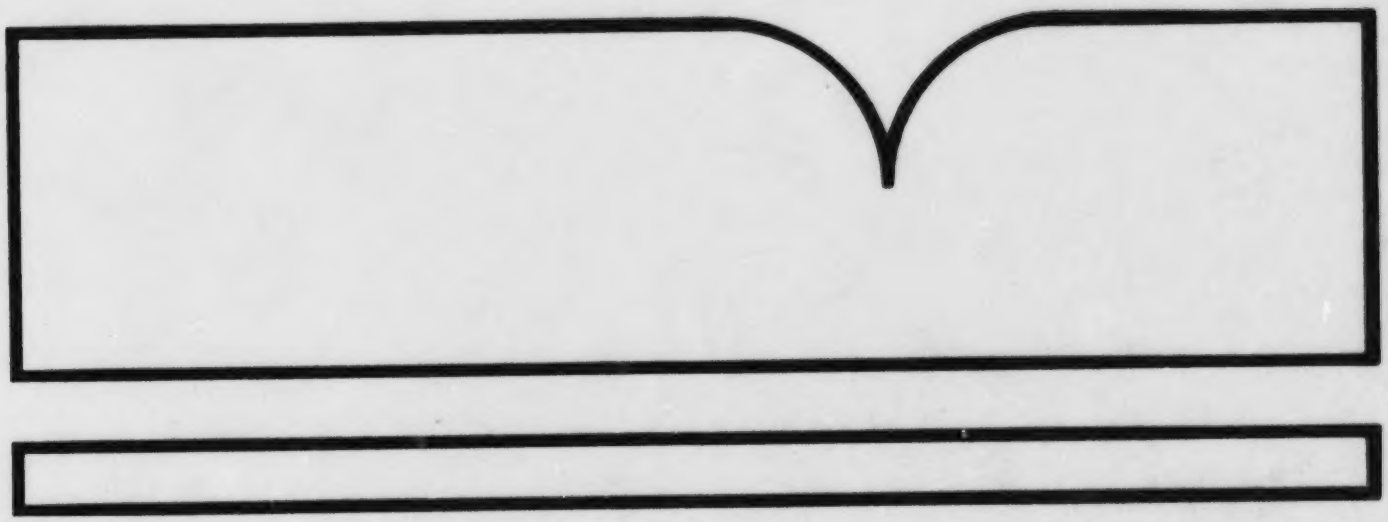

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16. ABSTRACT

This research program was initiated with the objective of evaluating a new process, the sulfide precipitation of heavy metals from industrial wastewaters. The process was expected to effect a more complete removal of heavy metals than conventional lime processing because of the much lower solubilities of metal sulfides than hydroxides.

Five processes were compared in bench-scale, continuous-flow equipment: conventional lime processing, conventional lime processing plus filtration, lime with a sulfide polishing and filtration, lime with sulfide, and lime with sulfide plus filtration.

Samples of actual wastewaters from 14 metal working industries (including Boeing) were processed through the bench-scale equipment using all five processes. Reductions in the concentrations of cadmium, chromium, copper, nickel, and zinc, plus selected other metals, were measured by atomic absorption chemical analysis.

Capital and operating costs for the five processes were compared for three plant sizes: 37.85 m^3/day (10,000 gal/day), 757 m^3/day (200,000 gal/day), and 1,893 m^3/day (500,000 gal/day).

The report recommends that, to reduce the levels of cadmium, copper, nickel, or zinc from a wastewater treatment plant using conventional lime processing, the addition of a final filtration should be considered first. If filtration does not achieve the desired low levels, then a sulfide polishing process with added filtration is recommended. If reduction of the levels of chromium, lead, silver, or tin is required, the conventional lime process plus filtration is recommended. The sulfide process did not significantly reduce the levels of these metals.

Details are included on the use of a specific ion electrode for the control of sulfide additions. The report does not include comparison testing of the commercial Sulfex process.

This report was submitted in fulfillment of Grant S805413 by Boeing under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from October 1977 to July 1979; work was completed as of July 1979.

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June 1980

SULFIDE PRECIPITATION OF HEAVY METALS

by

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory–Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report describes work undertaken to assess the merits of a method for removing heavy metals from wastewater by precipitation of the metals as sulfides instead of the usual hydroxide method. The results of the work can be used as a source of technical and cost data to compare the relative merits of the sulfide and hydroxide processes for removing heavy metals from industrial wastewaters.

David G. Stephan
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Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

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ABBREVIATIONS AND CONVERSIONS

ABBREVIATIONS

LO-CL	—lime only, clarified
LO-CLF	—lime only, clarified and filtered
LSPF	—lime, sulfide polished and filtered
LWS-CL	—lime with sulfide, clarified
LWS-CLF	—lime with sulfide, clarified and filtered
Bé	—Baumé degrees
v/v	—volume per volume ratio
μmho/cm	—micromho per centimeter (same as μS/cm)
L	—liter

METRIC CONVERSIONS

To Convert	To	Multiply by
gal	L	3.785 412 E+00
gal/min	L/min	3.785 412 E+00
gal/hr	L/h	3.785 412 E+00
gal/day	L/day	3.785 412 E+00
gal/mo	L/mo	3.785 412 E+00
inches	cm	2.540 000 E+00
lb/hr	kg/h	4.535 924 E-01
lb/day	kg/day	4.535 924 E-01
ppb	μg/L	1.000 000 E+00
ppm	mg/L	1.000 000 E+00

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SECTION 1

INTRODUCTION

The purification of industrial process wastewaters that contain heavy metals, such as cadmium, copper, chromium, nickel, and zinc, is commonly accomplished by precipitating these metals as hydroxides. The process is relatively inexpensive and is well established. However, removal of metals by the hydroxide process is incomplete, either because of slight solubility of the metal hydroxides or because of incomplete settling out of small particles of the hydroxides.

A much more complete removal of metals from wastewaters could be expected for processes using sulfides instead of hydroxides for precipitation. In general, metal sulfides have solubilities several orders of magnitude smaller than the corresponding hydroxides.

The work described in this report is a side-by-side comparison of three sulfide methods and two hydroxide methods of wastewater treatment. The tests were conducted on actual wastewaters from the nonferrous metal producing and metal finishing industry in the United States.

The wastewater treatments were conducted on a continuous-flow, bench-scale model treatment plant. The plant was of a size suitable for providing test runs lasting several hours from each 190L (50-gal) sample of wastewater.

The Permutit Company's Sulfex process (1, 2, 3), which uses an insoluble iron sulfide, originally was to be included in this study; however, legal difficulties prevented its inclusion.

This report is concerned only with soluble forms of sulfide precipitant, such as Na_2S, NaHS, and H_2S.

SECTION 2

CONCLUSIONS

OVERVIEW

Three sulfide precipitation processes that use soluble sulfides have been demonstrated (in a continuously operated bench-scale plant) as practical waste treatment processes for removing heavy metals from wastewater. The levels to which heavy metals can be reduced, and the costs of treatment compared to conventional lime treatment, are developed in this report.

The lime, sulfide polished and filtered (LSPF) process is the optimum sulfide process. For many wastewaters, treatment by the lime process followed by filtration is almost as effective as the LSPF process and costs far less.

EFFECTIVENESS OF PROCESSES FOR REMOVING HEAVY METALS

Based only on the reduction in concentration of five heavy metals (cadmium, chromium, copper, nickel, and zinc) in the effluents analyzed and without considering cost:

- The lime only, clarified (LO-CL) process is the least effective.
- Processes lime only, clarified and filtered (LO-CLF) and lime with sulfide, clarified (LWS-CL) are equally effective and better than the LO-CL process.
- Processes LSPF and lime with sulfide, clarified and filtered (LWS-CLF) are equally effective and better than any of the other three.

OPERATING AND CAPITAL EQUIPMENT COSTS

Each of the improvements to the basic LO-CL process carries a cost penalty. Tables 1 and 2 show that:

- The addition of a filtration operation (conversion to the LO-CLF process) adds from 0.4 to 0.7 percent to the operating costs and from 0.8 to 1.7 percent to the capital costs.
- The addition of a sulfide polishing operation, which includes filtration (conversion to the LSPF process), adds from 4.8 to 8.6 percent to the operating costs and from 8.6 to 11.6 percent to the capital costs.
- Conversion to a lime-with-sulfide process increases the capital cost by 6.2 to 11.6 percent; for a small plant, the process increases the operating cost by 7.1 to 7.8 percent, and for a medium or large plant, the process increases the operating cost by 26.4 to 39.5 percent.

TABLE 1. COMPARISON OF OPERATING COSTS

Operating cost of: / Plant capacity	Conventional lime plant with no filtration	Lime plant with filtration added (%)	Lime plant with sulfide "polish" operation, including filtration (%)	Lime-with-sulfide plant with no filtration (%)	Lime-with-sulfide plant with filtration added (%)
	LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
37.85 m^3/day (10,000 gal/day)	\$5.96/m^3 (\$22.6/1,000 gal)	+0.7	+4.8	+7.1	+7.8
757 m^3/day (200,000 gal/day)	\$0.90/m^3 (\$3.39/1,000 gal)	+0.4	+8.0	+26.4	+26.8
1,893 m^3/day (500,000 gal/day)	\$0.55/m^3 (\$2.08/1,000 gal)	+0.5	+8.6	+39.0	+39.5

TABLE 2. COMPARISON OF CAPITAL COSTS

Capital cost of: / Plant capacity	Conventional lime plant with no filtration	Lime plant with filtration added (%)	Lime plant with sulfide "polish" operation, including filtration (%)	Lime-with-sulfide plant with no filtration (%)	Lime-with-sulfide plant with filtration added (%)
	LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
37.85 m^3/day (10,000 gal/day)	\$233,000	+1.7	+11.6	+9.4	+11.6
757 m^3/day (200,000 gal/day)	\$799,000	+0.8	+11.6	+9.1	+10.0
1,893 m^3/day (500,000 gal/day)	\$1,296,000	+1.1	+8.6	+6.2	+7.2

SLUDGE DISPOSAL COSTS

The costs developed here include estimates for sludge disposal, which are based on the assumption that a sulfide sludge will not carry any significant cost penalty. At this stage, we do not know the additional surcharge, if any, that might be added to the disposal charges for a sulfide sludge.

EFFECTIVENESS OF SPECIFIC PROCESSES FOR REMOVING HEAVY METALS

The same order of preference as that given on page 2, with more details about individual metals, can be seen in Tables 3 and 4, which show the mean levels of the five metals before and after treatment.

The tables show that cadmium, copper, and zinc follow the same hierarchy as we established on page 2; that is, LO-CL is least effective, LO-CLF and LWS-CL are more

effective, and LSPF and LWS-CLF are most effective. The logarithmic mean removal of these three metals is 96.3 percent or greater for the two most effective processes, with a logarithmic mean effluent concentration of less than 50 μg/L.

Nickel removal does not follow the established hierarchy completely; when the logarithmic means are considered, the five processes are roughly equivalent. When the arithmetic means are considered, the hierarchy is the same as that established for cadmium, copper, and zinc. The logarithmic mean nickel removal is 88.4 percent or

TABLE 3. ARITHMETIC MEAN INFLUENT AND EFFLUENT CONCENTRATIONS FOR THE FIVE PROCESSES

Concentrations in μg/L (values in parentheses are percentage reductions from raw feed)

Heavy metal	Raw feed	LO-CL	LO-CLF	LWS-CL	LSPF	LWS-CLF
Cadmium	4,805	144 (97.00)	103 (97.86)	25 (99.48)	13 (99.37)	8 (99.83)
Copper	4,136	963 (76.72)	673 (83.73)	521 (87.40)	96 (97.68)	70 (98.31)
Chromium	26,006	603 (97.68)	58 (99.78)	370 (98.58)	58 (99.78)	86 (99.67)
Nickel	18,617	2,021 (89.14)	1,561 (91.62)	1,506 (91.91)	652 (96.50)	751 (95.97)
Zinc	259,865	8,385 (96.77)	6,629 (97.45)	491 (99.81)	517 (99.80)	422 (99.84)

TABLE 4. LOGARITHMIC MEAN INFLUENT AND EFFLUENT CONCENTRATIONS FOR THE FIVE PROCESSES*

Concentrations in μg/L (values in parentheses are percentage reductions from raw feed)

Heavy metal	Raw feed	LO-CL	LO-CLF	LWS-CL	LSPF	LWS-CLF
Cadmium	135	31 (77.04)	18 (86.67)	8 (94.07)	5 (96.30)	4 (97.04)
Copper	673	109 (83.80)	63 (90.64)	49 (92.72)	21 (96.88)	16 (97.62)
Chromium	1,039	136 (86.91)	24 (97.69)	108 (89.61)	24 (97.69)	32 (96.92)
Nickel	976	156 (84.02)	118 (87.91)	155 (84.12)	93 (90.47)	113 (88.42)
Zinc	23,904	820 (96.57)	210 (99.12)	195 (99.18)	46 (99.81)	31 (99.87)

*Log average of x_1 through $x_n = \log^{-1}\left(\frac{\sum_1^n \log x}{n}\right)$

greater for the two most effective processes, and the logarithmic mean nickel level in the effluents is 113 μg/L or less.

Chromium removal is not significantly improved by the presence of sulfides. That is, the unfiltered effluents (LO-CL and LWS-CL processes) showed logarithmic mean concentrations that were about equal at 136 and 108 μg/L, and the logarithmic means for the filtered effluents (LO-CLF, LSPF, and LWS-CLF) were also about equal at 24, 24, and 32 μg/L, respectively. This grouping clearly indicates that filtration after clarification had exerted a marked effect. Logarithmic mean chromium removal rates are 86.9 percent or greater for the unfiltered effluents and 96.9 percent or greater for the filtered. Logarithmic mean chromium levels of 32 μg/L or less were obtained in the effluents from the filtered processes and 136 μg/L or less in the unfiltered.

These findings agree with the observation that chromium, unlike the other metals considered, precipitates a hydroxide, not a sulfide, in the presence of sulfide ions. Thus, no difference would be anticipated between the removal rates of hydroxides precipitated by lime and hydroxides precipitated by sulfides. The solubility constant of the hydroxide would govern in both cases.

Lead was removed effectively in some tests, such as Runs 5, 8, 14, and 15. In each of these, the removal efficiency is 96.6 percent or greater for all five processes. However, in many other runs, the efficiency of removal is poor, ranging from 0 to 77 percent. In two cases, Runs 1 and 4, a striking improvement was noted in the effluents from filtered processes compared with the effluents from unfiltered processes. In Run 1, the removal efficiency of the filtered process is 91.1 percent or greater, but virtually no removal took place in the unfiltered process. In Run 4, the filtered-process removal efficiency is 82 percent or greater, but the efficiency is only 30 to 64 percent for the unfiltered process. Further work is needed to determine the underlying causes of these variations in the effectiveness of the processes. Based on the present tests, for lead removal, the sulfide processes apparently have no advantage over the lime process.

When the sulfide processes are used, silver removal is not significantly different from conventional lime processing.

Tin is removed efficiently by all processes in Runs 3, 7, and 12, with greater than 95-percent removal efficiency. Runs 4 and 5 are less efficient, with removal ranging from 19 to 86 percent. The sulfide processes are no more efficient than the conventional lime processes.

CONTROL OF SULFIDE CONCENTRATION BY SPECIFIC ION ELECTRODE

The dependability of the sulfide specific ion electrodes that were used to control sulfide levels was excellent during the 6-month period while the bench-scale plant was in operation. Ruggedness, freedom from drift, and ease of electrode maintenance were roughly intermediate when compared to those of a typical combination pH electrode and to those of an oxidation-reduction-potential (ORP) probe.

SECTION 3

RECOMMENDATIONS

To use conventional lime processing for reducing the levels of cadmium, copper, nickel, or zinc in the effluent from a wastewater treatment plant, we recommend that:

a. The addition of a filtration operation should be considered;
b. If reduction of these heavy metals to the desired levels cannot be achieved by filtration alone, the use of the LSPF process described in this report should be considered.

Details about costs and about the anticipated levels that would be achieved by courses a and b are given in this report.

The LWS processes are recommended only for small plants (37.85 m^3/day or 10,000 gal/day), because of the high consumption of soluble sulfide. The high consumption results in prohibitive chemical costs in larger plants (757 m^3/day or 200,000 gal/day and larger).

If reduction of the levels of chromium, lead, silver, or tin in the effluent from a waste treatment plant that uses conventional lime processing is required, we recommend filtration. The sulfide processes tested in this study did not significantly reduce the levels of these metals and are not recommended.

Finally, we recommend that research be initiated to determine information about the leaching and about other characteristics of the sulfide sludges generated by the processes described in this report and to determine the availability of disposal sites for such sludges.

SECTION 4

DESCRIPTION OF THE LIME PROCESSES (LO-CL AND LO-CLF)

GENERAL

The lime process for removing heavy metals from wastewater consists essentially of raising the pH of the normally acid or neutral wastewater to a predetermined value that is within the range 8.0 to 11.0 pH. A lime slurry is added, and the resultant precipitate, containing the bulk of the heavy metals, is separated.

The lime process will not remove chromium in the form of chromates or dichromates (for example, hexavalent chromium Cr^{6+}), and it will not remove heavy metals complexed with cyanide. Therefore, when these ions are present in the wastewater, pretreatment is necessary to remove them. In this program, the methods used to remove hexavalent chromium and cyanides are described in Section 8.

OUTLINE OF LIME PROCESS

The sequence of unit operations for the lime process used in this work is shown in Figure 1. Notes on each operation are provided in the following paragraphs; a description of the actual test hardware is given in Section 9.

Input Filter

A filter (0.1 μm nominal) at the input made sure that a uniform sample, free from variable amounts of suspended matter, would be processed. The filter was for sample uniformity only and is not recommended for a full-sized industrial plant.

Lime Slurry

This was composed of a suspension of 50 g/L CaO, continuously stirred.

Flash Mix Tank

In this continuously stirred tank, the pH of the raw feed water was raised to a preselected value. (Criteria for selecting the pH are given in Appendix H.) The value was maintained at ±0.1 pH unit by metered additions of lime slurry that were controlled by a pH probe. Polyelectrolyte additions were made to the pH-adjusted stream at the exit of the flash mix tank.

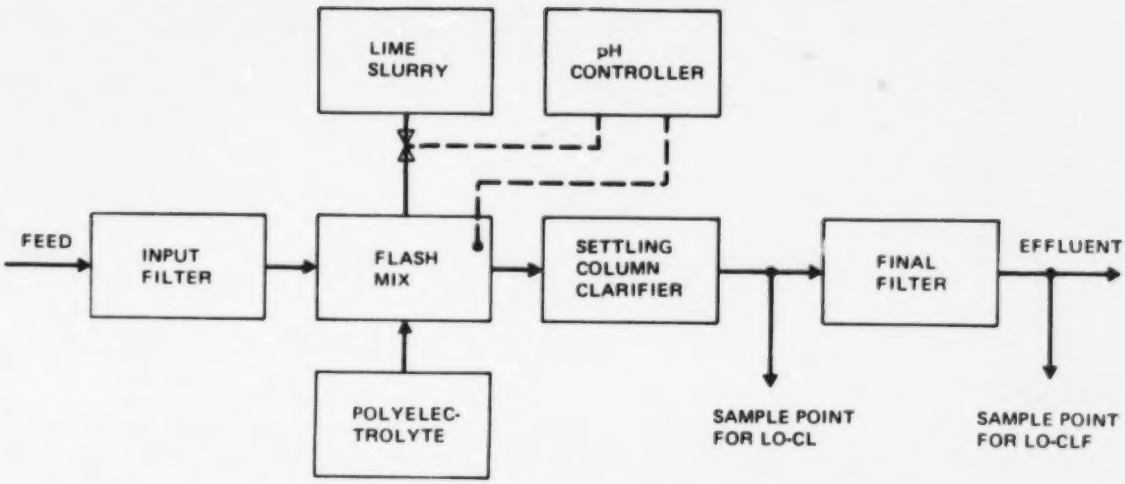


Figure 1. Lime only process flow diagram.

Polyelectrolyte

This substance was a freshly prepared concentrate of a proprietary, anionic polyelectrolyte that improves the flocculation of precipitated metals in wastewaters.

Settling Column Clarifier

The pH-adjusted wastewater from the flash mix tank was continuously fed upward through a settling column, and the precipitated sludge was allowed to collect at the bottom of the column. Clarified effluent was passed continuously from the top of the column. Liquid rise rate in the column was 10.3 mm/min, and the sludge settling velocity was generally 40 mm/min or greater; thus good separation was readily obtained. In all tests, except Runs 1, 2, and 9, sampling of the process effluents was delayed until a sludge bed at least 50 mm thick had formed; more complete clarification is expected when the effluent passes through such a bed. For Runs 1, 2, and 9, insufficient precipitate was generated, and it was impossible to build up a thick sludge bed with the limited 190L samples that were available.

Final Filter

A final filter (0.1 μm nominal) removed traces of precipitate that were carried over from the clarifier. Samples drawn from points before and after the filter were used to determine the amount of carryover; the LO-CL samples were taken before the filter, and the LO-CLF samples were taken after it.

SECTION 5

DESCRIPTION OF THE LIME-WITH-SULFIDE PROCESSES (LWS-CL AND LWS-CLF)

GENERAL

The lime-with-sulfide process for removing heavy metals from wastewater is a modification of the lime process described in Section 4. In the modified process, sulfide is added to the flash mix tank simultaneously with the lime slurry. Coprecipitation of heavy metal sulfides and hydroxides occurs in the tank.

For each wastewater in this study, the same pH value was used for the lime process and the lime-with-sulfide process.

Sulfide additions were made continuously to the flash mix tank to maintain a small (about 0.5 mg/L) excess of $S^=$.

OUTLINE OF LIME-WITH-SULFIDE PROCESS

The sequence of unit operations of the lime-with-sulfide process, shown in Figure 2, involves sulfide additions controlled by a specific ion electrode. Soluble sulfide is added to the flash mix tank simultaneously with the lime slurry. The input filter, lime slurry, polyelectrolyte, clarifier, and final filter were operated in the same manner as in the lime process (see Section 4). A description of the additional test hardware is given in Section 9. Notes on the additional operation and the flash mix tank are provided in the following paragraphs.

Soluble Sulfide

This was composed of a freshly prepared solution of 10 g/L $Na_2S{\cdot}9H_2O$.

Flash Mix Tank

Metered additions of lime slurry and sulfide solution were made to the raw feed water in this continuously stirred tank. The pH of the raw feed water was raised to a preselected value. (Criteria for selecting the pH are given in Appendix H.) The value was maintained at ±0.1 pH unit by metered additions of the lime slurry, as controlled by the pH probe. Simultaneously, metered additions of the sulfide solution, which were controlled by a reference electrode pair to detect the sulfide specific ion, maintained a preselected potential of -550 mV ±10 mV with respect to the reference electrode. Polyelectrolyte additions were made to the pH- and sulfide-adjusted stream at the exit of the flash mix tank.

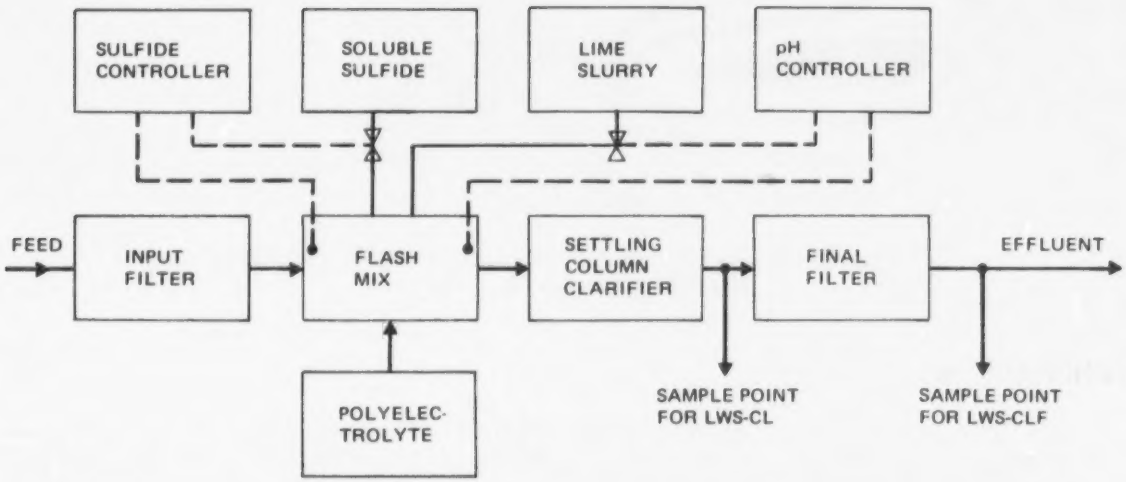


Figure 2. Lime-with-sulfide process flow diagram.

CONTROL OF SULFIDE ADDITIONS

The preselected value of -550 mV corresponds to about 0.5 mg/L of free sulfide and was selected for two reasons:

- The curve of electrical potential versus sulfide concentration has its maximum gradient in this region, thus giving a large response to a small change in free-sulfide concentration.
- The concentration of 0.5 mg/L was the minimum excess sulfide that gave no detectable odor from solutions at pH 8 to 9.

The electrode was nearly troublefree and had negligible drift. Fouling of the electrode surface by precipitated materials usually was countered by wiping with a paper tissue. At about 2-month intervals, the response of the electrode became noticeably sluggish when tested in a reference solution. Light abrasion with 600-mesh silicon carbide corrected this condition and restored the response rate. The electrode usually was used for 6 hours per day and stored overnight in clean water.

SECTION 6

DESCRIPTION OF THE LIME, SULFIDE POLISHED AND FILTERED PROCESS (LSPF)

GENERAL

The lime, sulfide polished and filtered process for removing heavy metals from wastewater is a modification of the lime process described in Section 4. In the modified process, sulfide is added to the wastewater after the bulk of the heavy metals has been removed by a lime process. The precipitation and removal of the small amount of heavy metals that remain after lime processing is the polishing operation.

OUTLINE OF LIME, SULFIDE POLISHED AND FILTERED PROCESS

The sequence of unit operations of the lime, sulfide polished and filtered process, shown in Figure 3, involves sulfide additions, controlled by a specific ion electrode, to the sulfide polishing tank, which contains lime-processed and clarified wastewater. The input filter, lime slurry, polyelectrolyte, clarifier, and final filter were operated in the same manner as they were in the lime process (see Section 4). A description of the additional test hardware used in this process is given in Section 9. Notes on the sulfide polishing operation are provided in the following paragraphs.

Soluble Sulfide

This was composed of a freshly prepared solution of 10 g/L $Na_2S \cdot 9H_2O$.

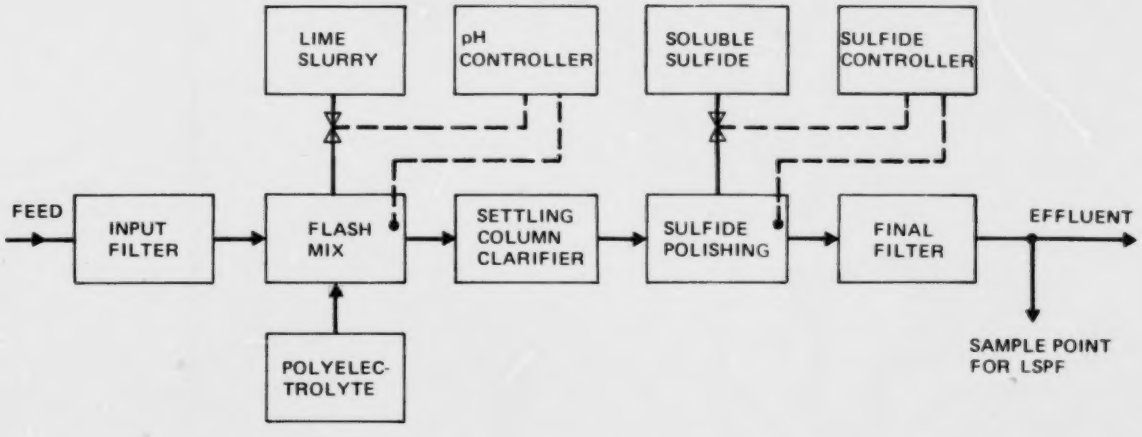


Figure 3. Lime, sulfide polished and filtered process flow diagram.

Sulfide Polishing

Metered additions of the soluble sulfide solution were made to the pH-adjusted and clarified wastewater in this continuously stirred tank. The metered additions, which were controlled by a reference electrode pair to detect the sulfide specific ion, maintained a preselected potential of -550 mV ±10 mV with respect to the reference electrode. The behavior of the electrodes was similar to their behavior in the LWS process. The notes in Section 5 under "Control of Sulfide Additions" apply also to the LSPF process.

SECTION 7

REASON FOR OMISSION OF TESTS ON THE SULFEX PROCESS

The Sulfex process for removing heavy metals from processed waste streams by sulfide precipitation is a proprietary system developed by The Permutit Company (2). It differs from others described in Sections 5 and 6 of this report in that it uses relatively insoluble iron sulfide, instead of highly soluble sodium sulfite or hydrosulfide, as its source of sulfide ions for precipitation. Descriptions of the Sulfex process are given in References 1, 2, and 3.

Although we originally intended to include the Sulfex process in this study, to enable its merits to be objectively determined in direct comparison with conventional lime and soluble sulfide methods, problems with commercial secrecy prevented its inclusion in the program.

The Sulfex process relies partly on an existing patent (4) and partly on commercially secret knowledge, some of which is included in a new patent application. The Permutit Company understandably declined to reveal details of their process until an acceptable secrecy agreement had been signed between Permutit and Boeing. Protracted negotiations failed to reach this agreement, and the comparative tests on this process were deleted from the program.

SECTION 8

REMOVAL OF CYANIDES AND HEXAVALENT CHROMIUM FROM WASTEWATERS

GENERAL

Heavy metals complexed with cyanides are not removed by the lime process, and neither is chromium in the form of chromates and dichromates, that is, hexavalent chromium (5). Consequently, the removal of cyanides and hexavalent chromium from a wastewater before subsequent lime processing is a common practice.

REMOVAL OF CYANIDES

The alkaline chlorination process (5, 6) was used to remove cyanides when they were present in the raw wastewater, that is, in Runs 5 and 9. The process, which was carried out in 100L batches, is as follows:

a. Raise pH to 10.0 or higher (not necessary with the samples for Runs 5 and 9 because they were already in this condition).
b. Add 5-percent sodium hypochlorite solution until oxidizing conditions are present, as indicated by an oxidation-reduction potential (ORP) (7) of 400 mV minimum to convert the cyanide to cyanate.
c. Reduce pH to 2.5 by the addition of sulfuric acid. After about 5 min, the cyanates in the wastewater are converted to carbon dioxide and nitrogen.

REMOVAL OF HEXAVALENT CHROMIUM

Reduction of the hexavalent chromium found in all raw feed wastewaters (except Runs 5, 8, 12, and 13) was accomplished by adding sulfuric acid wherever necessary to lower the pH to 2.5. This was followed by the addition of sodium sulfite until a 10- to 15-mg/L excess of SO_3 was indicated by iodometric titration (8). The wastewater was allowed to stand for a minimum of 1 hour after reduction before treatment in the bench-scale plant.

SECTION 9

BENCH-SCALE EQUIPMENT USED IN THE TESTS

GENERAL

Wastewaters were processed through a single bench-scale unit (Figure 4) that was capable of operation in each of the five process modes: LO-CL, LO-CLF, LSPF, LWS-CL, and LWS-CLF. Changeover from one mode to another was accomplished by opening the appropriate valves and actuating the necessary feed pumps. Wastewater flow rate through the equipment was 130 mL per minute.

Process details are given in Sections 4 (lime process), 5 (lime-with-sulfide process), and 6 (lime, sulfide polished and filtered process). Figure 5 is a flow diagram for the multipurpose bench-scale unit. Figures 4, 6, and 7 show the actual equipment.

EQUIPMENT DETAILS

Individual items of equipment are detailed in the following list (located by key number in the flow diagram, Figure 5).

1. Sample drum: ACT 1 poly-drum (black, polyethylene, 55-gal shipping and storage drum); ACT Poly-drum Division, 1100 South Azusa Ave., City of Industry, California 91748
2. Tank: 350L stainless steel
3. Stirrer: ½ hp, 1,725 rpm, 32-in stainless steel shaft, with propeller
4. Tank: Polyethylene, 150L, with lid
5. Pump: Peristaltic type, 130 mL per minute
6. Filter: Disposable, wound polypropylene fiber type, nominal removal rating 0.1 µm; Motor Guard Corporation Model D-15, P. O. Box 1834, San Leandro, California 94577
7. Pump: Peristaltic type, variable speed 6 to 120 mL per minute, Masterflex 7545 drive and 7014 pump head; Cole-Parmer Industrial Co., 7425 N. Oak Park Ave., Chicago, Illinois 60648
8. Tank: Polyethylene, 7.5L capacity
9. pH controller: Chemtrix type 45 with 500W output and high and low adjustable setpoints; Chemtrix Inc., 163 S.W. Freeman Ave., Hillsboro, Oregon 97123
10. Sulfide controller: Chemtrix type 45 with 400W output and high and low adjustable setpoints; Chemtrix Inc., 163 S.W. Freeman Ave., Hillsboro, Oregon 97123
11. Tank: Polyethylene, 3L capacity
12. Clarifier: Plexiglas column, 127-mm (5-in) diameter, 610-mm (24-in) water height

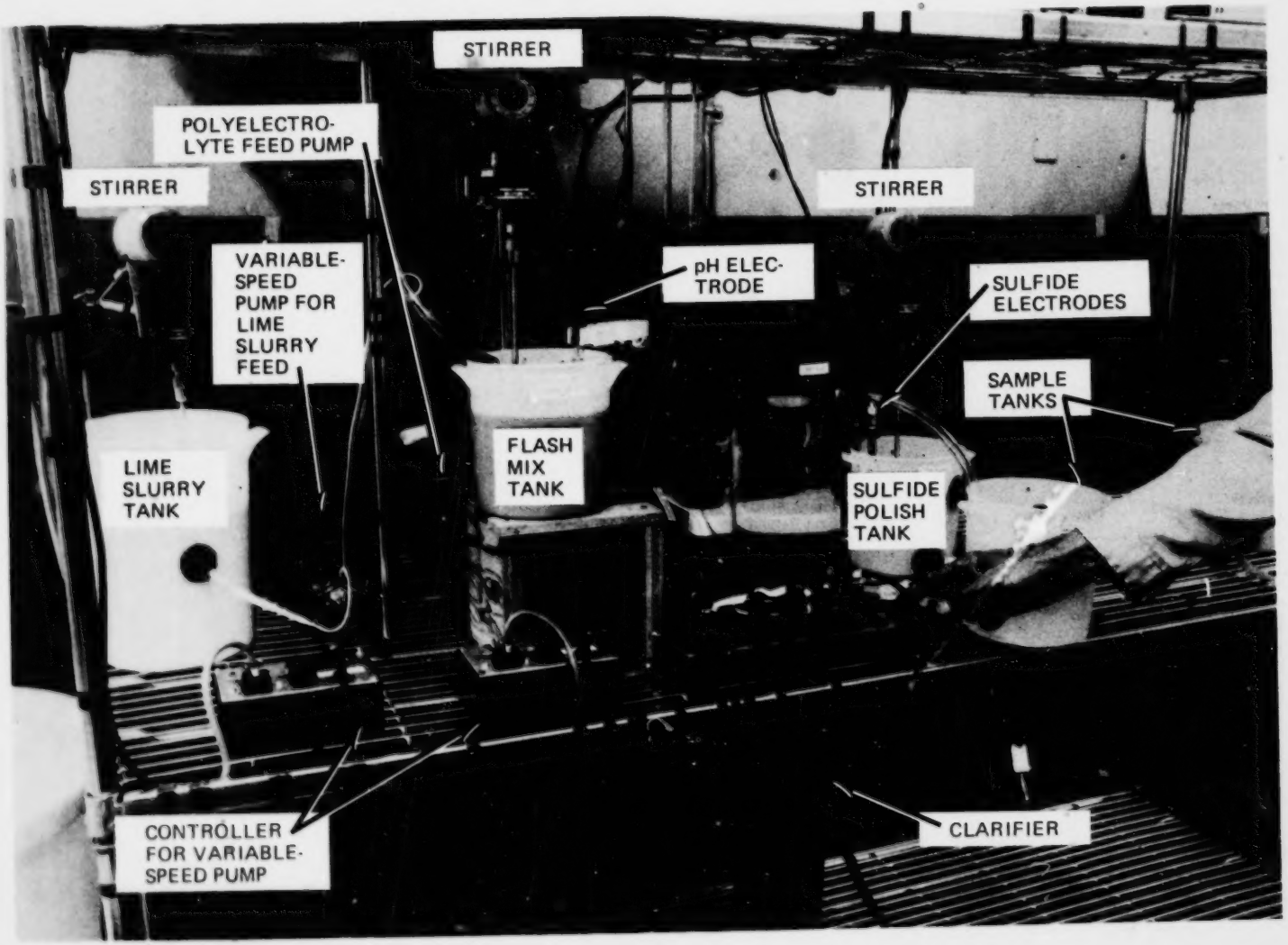
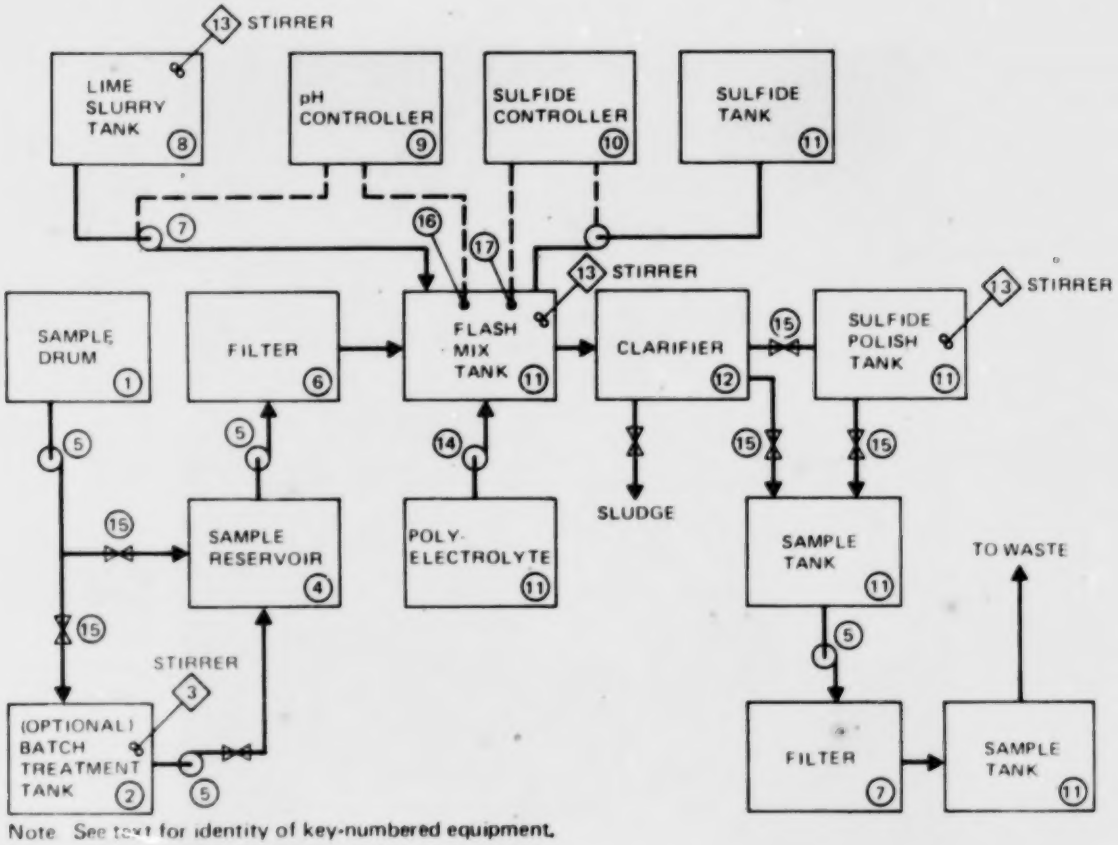


Figure 4. Bench-scale unit for processing industrial wastewater by the LO-CL, LO-CLF, LSPF, LWS-CL, and LWS-CLF processes.



Note: See text for identity of key-numbered equipment.

Figure 5. Flow diagram of multipurpose bench-scale equipment.

13. Stirrer: Variable-speed laboratory stirrer, 1/75 hp, with 50-mm-diameter stainless steel propeller, T-Line No. 101, Tallboys Engineering Corporation, Emerson, New Jersey 07630
14. Pump: Peristaltic type, 2.8 mL per minute; Cole-Parmer Industrial Co., 7425 N. Oak Park Ave., Chicago, Illinois 60648
15. Valve: Pinch-type tubing control valve, Dura-Clamp®, United States Plastic Corporation, Lima, Ohio 45801
16. pH electrode: Chemtrix, No. H005; Chemtrix Inc., 163 S.W. Freeman Ave., Hillsboro, Oregon 97123
17. Sulfide specific ion electrode: Orion 94-16A used with reference electrode Orion 90-02, Orion Research Inc., 380 Putnam Ave., Cambridge, Massachusetts 02139; or, Sensorex S1015M used with reference electrode, Sensorex RD1015F, Sensorex, 502 Armstrong Ave., Irvine, California 92705

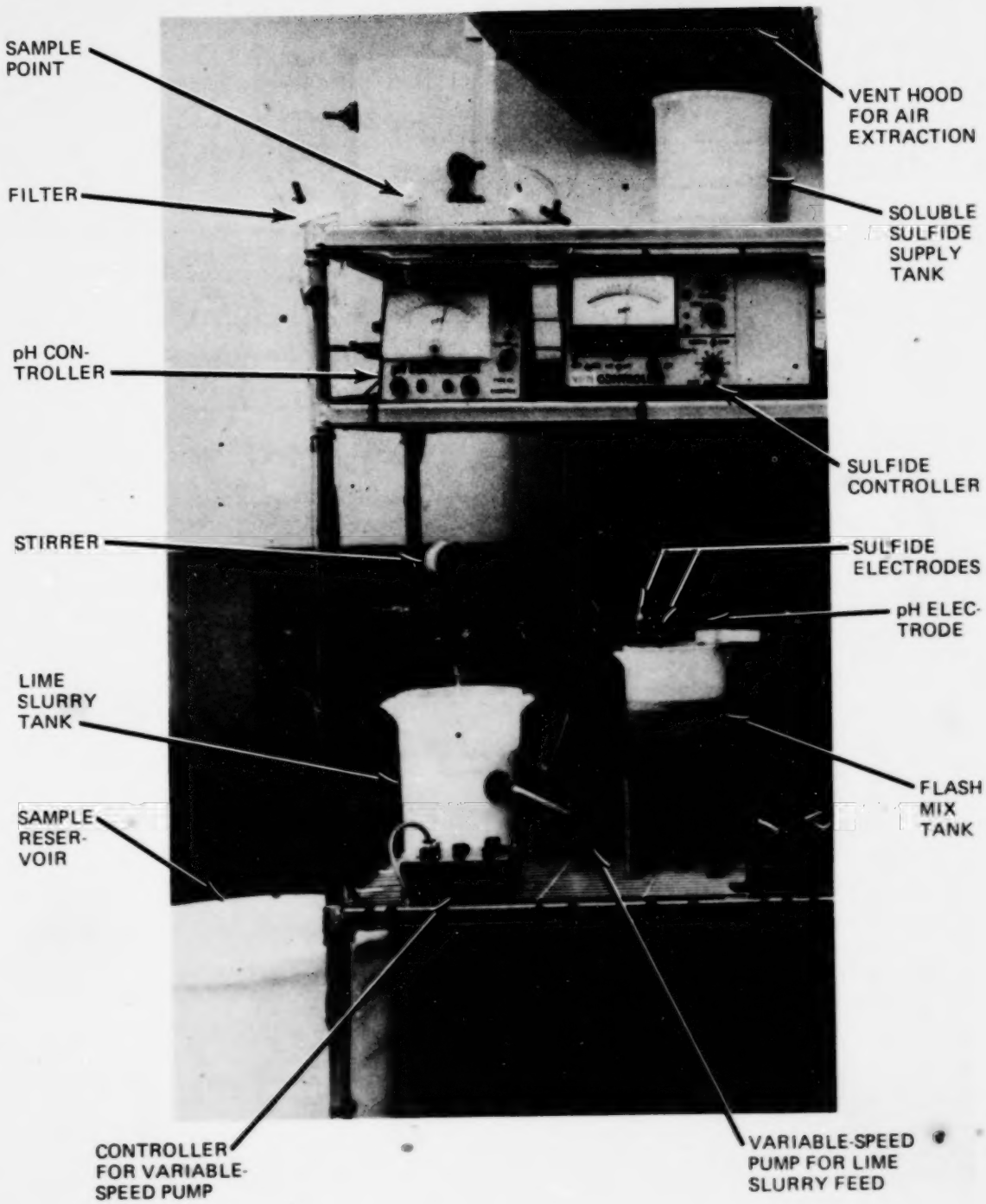


Figure 6. Bench-scale unit showing instrumentation and air vent hood.

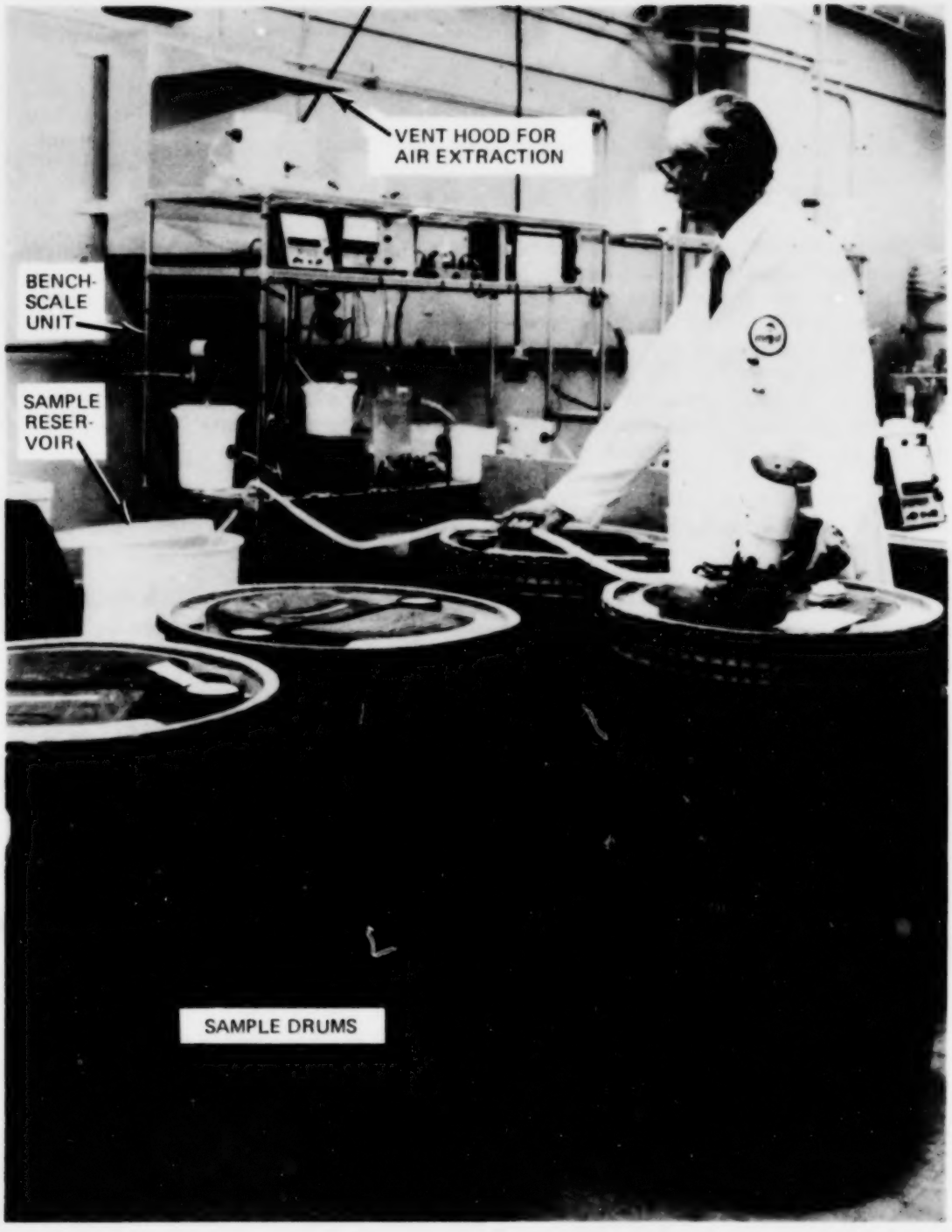


Figure 7. Wastewater being charged into sample reservior of bench-scale unit from sample drum.

SECTION 10

DESCRIPTION OF THE FOURTEEN WASTEWATERS TREATED

The wastewaters collected for treatment in the bench scale plant were representative of wastewaters generated by the nonferrous metal producing and metal finishing industries in the United States. Because the chelating agents usually present in electroplating wastewater are known to inhibit precipitation (9, 10), emphasis was placed on obtaining wastewater samples from as wide a variety of electroplating sources as possible. Twelve samples of electroplating, anodizing, and other metal finishing rinse waters plus one nonferrous metal smelter's wastewater (Run 8) and one copper printed circuit etching wastewater were collected. All the samples were collected in new polyethylene 190L (50-gal) drums.

The samples were supplied from companies spread over 10 states to minimize the effects of local geographical conditions. About half of the samples were average samples collected over a few days; the remainder were "grab" samples.

Brief individual descriptions of each sample are given in Appendix A (case history data); the identity of the wastewater supplier companies is kept confidential at their request.

SECTION 11

PRESENTATION OF THE ANALYTICAL RESULTS

To simplify the data on the efficiency of removing heavy metals by the five processes, the detailed results of Appendix A are condensed into two tables and a number of graphic presentations.

Tables 5 and 6 show the mean concentrations of cadmium, copper, chromium, nickel, and zinc in the raw feed and in the effluents from each of the processes. Conventional mean determinations may be misleading when applied to sets having an extremely wide range (such as the nickel effluent concentrations, which range from 4 to 11,000 μg/L for one process). Thus, both the conventional mean and the logarithmic mean are used. Table 5 shows the conventional mean, and Table 6, the mean based on a logarithmic scale. That is, for n observations ($x_1 \ldots\ldots x_n$):

$$\text{Conventional (arithmetic) mean} = \frac{\Sigma_1^n x}{n}$$

$$\text{Logarithmic mean} = \log^{-1}\left(\frac{\Sigma_1^n \log x}{n}\right)$$

Tables 5 and 6 also show the percentage reduction of the heavy metal concentrations for each process.

TABLE 5. ARITHMETIC MEAN INFLUENT AND EFFLUENT CONCENTRATIONS FOR THE FIVE PROCESSES

Concentrations in μg/L (values in parentheses are percentage reductions from raw feed)

Heavy metal	Raw feed	LO-CL	LO-CLF	LWS-CL	LSPF	LWS-CLF
Cadmium	4,805	144 (97.00)	103 (97.86)	25 (99.48)	13 (99.37)	8 (99.83)
Copper	4,136	963 (76.72)	673 (83.73)	521 (87.40)	96 (97.68)	70 (98.31)
Chromium	26,006	603 (97.68)	58 (99.78)	370 (98.58)	58 (99.78)	86 (99.67)
Nickel	18,617	2,021 (89.14)	1,561 (91.62)	1,506 (91.91)	652 (96.50)	751 (95.97)
Zinc	259,865	8,385 (96.77)	6,629 (97.45)	491 (99.81)	517 (99.80)	422 (99.84)

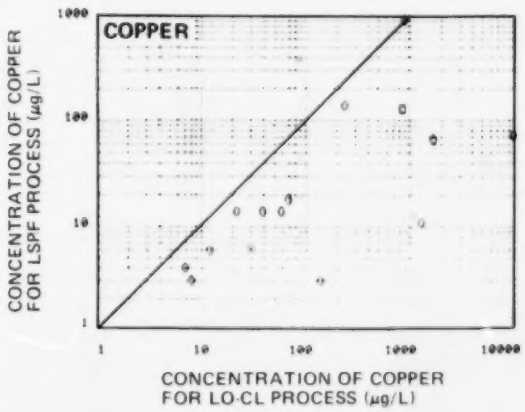
TABLE 6. LOGARITHMIC MEAN* INFLUENT AND EFFLUENT CONCENTRATIONS FOR THE FIVE PROCESSES

Concentrations in μg/L (values in parentheses are percentage reductions from raw feed)

Heavy metal	Raw feed	LO-CL	LO-CLF	LWS-CL	LSPF	LWS-CLF
Cadmium	135	31 (77.04)	18 (86.67)	8 (94.07)	5 (96.30)	4 (97.04)
Copper	673	109 (83.80)	63 (90.64)	49 (92.72)	21 (96.88)	16 (97.62)
Chromium	1,039	136 (86.91)	24 (97.69)	108 (89.61)	24 (97.69)	32 (96.92)
Nickel	976	156 (84.02)	118 (87.91)	155 (84.12)	93 (90.47)	113 (88.42)
Zinc	23,904	820 (96.57)	210 (99.12)	195 (99.18)	46 (99.81)	31 (99.87)

*Log average of x_1 through $x_n = \log^{-1}\left(\frac{\sum_1^n \log x}{n}\right)$

Two main types of graphic plots are given in the Appendices. Appendix C plots compare the effluent concentrations of pairs of processes. Each point plotted has two coordinates: the concentration of a metal in process A effluent (x-axis), and the concentration of the same metal in process B effluent (y-axis). A point below the 45-deg line results when there is a higher concentration of the metal in process A effluent; if all the points are below the line, then process A is clearly less effective in removing that metal than process B. For example, in the following diagram the LO-CL process is less effective than the LSPF process in removing copper.

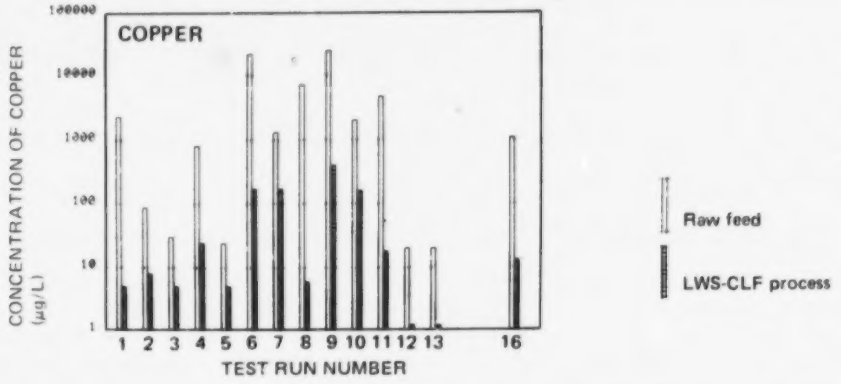


The paired comparisons of Appendix C are as follows:

C-1 diagrams compare the LO-CL and LSPF processes for cadmium, copper, chromium, nickel, and zinc

C-2 diagrams compare the LO-CLF and LO-CL processes
C-3 diagrams compare the LSPF and LWS-CL processes
C-4 diagrams compare the LWS-CL and LO-CLF processes
C-5 diagrams compare the LO-CLF and LWS-CLF processes
C-6 diagrams compare the LO-CL and LWS-CLF processes
C-7 diagrams compare the LSPF and LO-CLF processes
C-8 diagrams compare the LWS-CLF and LSPF processes
C-9 diagrams compare the LWS-CLF and LWS-CL processes
C-10 diagrams compare the LWS-CL and LO-CL processes

Appendix G bar charts show the relationship between the raw feed concentrations and effluent concentrations for each heavy metal. For example, the following bar chart shows raw feed and effluent concentrations for copper in the LWS-CLF process.



The bar charts of Appendix G are as follows:

G-1 diagrams display raw feed and effluent concentrations of cadmium, copper, chromium, nickel, and zinc for the LO-CL process
G-2 diagrams display raw feed and effluent concentrations for the LO-CLF process
G-3 diagrams display raw feed and effluent concentrations for the LSPF process
G-4 diagrams display raw feed and effluent concentrations for the LWS-CL process
G-5 diagrams display raw feed and effluent concentrations for the LWS-CLF process

The use of the graphic presentations of Appendices C and G enables rapid visual comparisons to be made for any desired sets of the experimental results.

SECTION 12

CAPITAL COSTS OF FULL-SCALE PLANTS

The estimated costs of installing full-scale wastewater treatment plants are given in this section. Not included in the estimates are: land acquisition costs; sewer, road, and other utility connection costs; preparation costs for environmental impact statement; or site survey and test boring costs.

Table 7 compares the estimated capital costs of small, medium-sized, and large plants for the five treatment processes.

Tables 8, 9, and 10 are detailed cost estimate summaries for constructing plants for each of the five processes.

TABLE 7. SUMMARY OF PLANT CAPITAL INSTALLATION COSTS

Process / Plant capacity	Capital costs (thousands of 1978 dollars)				
	LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
37.85 m^3/day (10,000 gal/day)	233	237	259	255	259
757 m^3/day (200,000 gal/day)	799	805	892	872	879
1,893 m^3/day (500,000 gal/day)	1,296	1,310	1,407	1,376	1,389

TABLE 8. SMALL PLANT CONSTRUCTION COSTS

Plant capacity = 37.85 m^3 (10,000 gal) per day

Item	Capital	Expense	Total
Process 1, LO-CL			
Architectural	$ 42,700	$5,400	$ 48,100
Mechanical	139,500		139,500
Electrical	19,000		19,000
Subtotal	$201,200	$5,400	$206,600
A&E fee + CM,* 12.5%	25,200	700	25,900
Total	$226,400	$6,100	$232,500
Process 2, LO-CLF			
Architectural	$ 43,464	$5,400	$ 48,864
Mechanical	141,996		141,996
Electrical	19,340		19,340
Subtotal	$204,800	$5,400	$210,200
A&E fee + CM,* 12.5%	25,600	700	26,300
Total	$230,400	$6,100	$236,500
Process 3, LSPF			
Architectural	$ 52,100	$6,400	$ 58,500
Mechanical	152,300		152,300
Electrical	19,000		19,000
Subtotal	$223,400	$6,400	$229,800
A&E fee + CM,* 12.5%	27,900	800	28,700
Total	$251,300	$7,200	$258,500
Process 4, LWS-CL			
Architectural	$ 52,100	$6,400	$ 58,500
Mechanical	148,800		148,800
Electrical	19,000		19,000
Subtotal	$219,900	$6,400	$226,300
A&E fee + CM,* 12.5%	27,500	800	28,300
Total	$247,400	$7,200	$254,600
Process 5, LWS-CLF			
Architectural	$ 52,945	$6,400	$ 59,345
Mechanical	151,214		151,214
Electrical	19,308		19,308
Subtotal	$223,467	$6,400	$229,867
A&E fee + CM,* 12.5%	27,933	800	28,733
Total	$251,400	$7,200	$258,600

*A&E fee + CM = architectural and engineering fee plus central management

TABLE 9. MEDIUM-SIZED PLANT CONSTRUCTION COSTS

Plant capacity = 757 m^3 (200,000 gal) per day

Item	Capital	Expense	Total
Process 1, LO-CL			
Architectural	$287,400	$3,800	$291,200
Mechanical	326,900		326,900
Electrical	91,700		91,700
Subtotal	$706,000	$3,800	$709,800
A&E fee + CM,* 12.5%	88,300	400	88,700
Total	$794,300	$4,200	$798,500
Process 2, LO-CLF			
Architectural	$289,770	$3,800	$293,570
Mechanical	329,596		329,596
Electrical	92,456		92,456
Subtotal	$711,822	$3,800	$715,622
A&E fee + CM,* 12.5%	88,978	400	89,378
Total	$800,800	$4,200	$805,000
Process 3, LSPF			
Architectural	$296,800	$3,800	$300,600
Mechanical	373,500		373,500
Electrical	118,800		118,800
Subtotal	$789,100	$3,800	$792,900
A&E fee + CM,* 12.5%	98,600	400	99,000
Total	$887,700	$4,200	$891,900
Process 4, LWS-CL			
Architectural	$296,800	$3,800	$300,600
Mechanical	361,200		361,200
Electrical	113,600		113,600
Subtotal	$771,600	$3,800	$775,400
A&E fee + CM,* 12.5%	96,600	400	97,000
Total	$868,200	$4,200	$872,400
Process 5, LWS-CLF			
Architectural	$299,074	$3,800	$302,874
Mechanical	363,967		363,967
Electrical	114,470		114,470
Subtotal	$777,511	$3,800	$781,311
A&E fee + CM,* 12.5%	97,189	400	97,589
Total	$874,700	$4,200	$878,900

Note: Piling costs for medium-sized plants represent 12% to 16% of the total cost.

*A&E fee + CM = architectural and engineering fee plus central management

TABLE 10. LARGE PLANT CONSTRUCTION COSTS

Plant capacity = 1,893 m^3 (500,000 gal) per day

Item	Capital	Expense	Total
Process 1, LO-CL			
Architectural	$621,800	$11,300	$633,100
Mechanical	425,200		425,200
Electrical	93,900		93,900
Subtotal	$1,140,900	$11,300	$1,152,200
A&E fee + CM,* 12.5%	142,600	1,400	144,000
Total	$1,283,500	$12,700	$1,296,200
Process 2, LO-CLF			
Architectural	$628,343	$11,300	$639,643
Mechanical	429,674		429,674
Electrical	94,872		94,872
Subtotal	$1,152,889	$11,300	$1,164,189
A&E fee + CM,* 12.5%	144,111	1,400	145,511
Total	$1,297,000	$12,700	$1,309,700
Process 3, LSPF			
Architectural	$631,200	$11,300	$642,500
Mechanical	487,000		487,000
Electrical	121,000		121,000
Subtotal	$1,239,200	$11,300	$1,250,500
A&E fee + CM,* 12.5%	154,900	1,400	156,300
Total	$1,394,100	$12,700	$1,406,800
Process 4, LWS-CL			
Architectural	$631,200	$11,300	$642,500
Mechanical	464,700		464,700
Electrical	115,800		115,800
Subtotal	$1,211,700	$11,300	$1,223,000
A&E fee + CM,* 12.5%	151,500	1,400	152,900
Total	$1,363,200	$12,700	$1,375,900
Process 5, LWS-CLF			
Architectural	$637,468	$11,300	$648,768
Mechanical	469,315		469,315
Electrical	116,950		116,950
Subtotal	$1,223,733	$11,300	$1,235,033
A&E fee + CM,* 12.5%	152,967	1,400	154,367
Total	$1,367,700	$12,700	$1,389,400

Note: Piling costs for large plants represent 12% to 16% of the total cost.

*A&E fee + CM = architectural and engineering fee plus central management

SECTION 13

OPERATING COSTS OF FULL-SCALE PLANTS

GENERAL

Operating costs for three full-scale plants based on the principles of the bench-scale plants is developed in this section. A summary of the operating costs is presented in Table 11. Details on which the costs are based are given in Tables 12, 13, and 14.

ASSUMPTIONS USED IN THE CALCULATIONS

a. All costs are in 1978 dollars.

b. Amortization of plant cost (purchase price plus installation cost) is calculated at 8 percent over a 12-year life.

c. Operating labor costs are $30/hr total, including basic wage, overtime, fringe benefits, and management and overhead burden.

d. One operator working half of an 8-hr shift will be required for the smallest plant, 37.85 m^3/day (10,000 gal/day). Three part-time operators (with total labor of 8 man-hours per day), will be required for each of the larger plants, at 757 m^3/day (200,000 gal/day), and 1,893 m^3/day (500,000 gal/day). A three-shift operating schedule increases the total operating labor cost but allows a reduction in capital equipment cost (the major cost item); the equipment can be sized to handle one-third of the load of a single-shift operation.

TABLE 11. SUMMARY OF OPERATING COSTS

Process / Plant capacity	Operating cost, $/$m^3$ ($/1,000 gal)				
	LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
37.85 m^3/day (10,000 gal/day)	5.96 (22.57)	6.00 (22.72)	6.24 (23.65)	6.38 (24.17)	6.42 (24.32)
757 m^3/day (200,000 gal/day)	0.90 (3.40)	0.90 (3.42)	0.97 (3.68)	1.13 (4.30)	1.14 (4.32)
1,893 m^3/day (500,000 gal/day)	0.55 (2.08)	0.55 (2.09)	0.60 (2.26)	0.76 (2.89)	0.77 (2.90)

e. The following items are not taken into account in this study: startup costs, operating profit, site purchase cost, preparation costs for environmental impact statement, sewage disposal charges, tax credits, costs of cyanide destruction in the case of wastewaters that contain cyanides, special additives (such as antifoaming agents), electric power costs, and laboratory chemical analysis charges.

f. Costs of process consumables (for example, lime, sulfide) are based on the average value of each consumable required for the 14 wastewaters, at prices published in Chemical Marketing Reporter for December 4, 1978 (12). These prices are:

Sulfuric acid, 66 Bé	$ 49.41/ton
Sodium sulfite anhydrous, technical*	$ 13.75/100 lb
Lime, pebble quicklime	$ 31.88/ton
Sodium hydrosulfide, 71 percent*	$305.00/ton
Polyelectrolyte, Betz Laboratories No. 1110	$ 2.55/lb

* For calculations in this report, sodium sulfite and sodium hydrosulfide are assumed to be used in full-scale plants. Cost savings might accrue through the use of equivalent forms of these reactants. For example, many treatment plants use sulfur dioxide acquired in cylinders instead of sodium sulfite. Hydrogen sulfide in cylinders, though considerably less costly ($0.24/kg of sulfur) than sodium hydrosulfide ($0.827/kg of sulfur), would incur extensive development costs (to overcome potential mass transfer problems) and would increase equipment costs (to preclude release to the atmosphere). For handling convenience, sodium sulfite Na_2SO_3 and sodium sulfide $Na_2S{\cdot}9H_2O$ were used in the laboratory.

TABLE 12. OPERATING COSTS FOR SMALL PLANT

Plant capacity = 37.85 m^3/day (10,000 gal/day)	Cost per day ($)				
	LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
Equipment amortization*	88.15	89.66	98.00	96.53	98.04
Operating labor †	120.00	120.00	120.00	120.00	120.00
Chemicals ‡	4.35	4.35	5.29	11.96	11.96
Maintenance**	12.00	12.00	12.00	12.00	12.00
Sludge disposal††	1.16	1.16	1.16	1.16	1.16
Totals	225.66	227.17	236.45	241.65	243.16

* Equipment amortization ‡‡

(LO-CL)	$232,500	x	0.132695 / 350 days	=	$88.15 per day
(LO-CLF)	236,500	x	0.132695 / 350 days	=	89.66 per day
(LSPF)	258,500	x	0.132695 / 350 days	=	98.00 per day
(LWS-CL)	254,600	x	0.132695 / 350 days	=	96.53 per day
(LWS-CLF)	258,600	x	0.132695 / 350 days	=	98.04 per day

† Operating labor: $30/hr x 4 hr/day = $120.00 per day

‡ Chemicals

		Cost per day ($)		
		LO-CL, LO-CLF	LSPF	LWS-CL, LWS-CLF
Sulfuric acid:	290 mg/L x $0.0507/kg x 37.85 m^3/day =	0.55	0.55	0.55
Sodium sulfite:	120 mg/L x $0.280/kg x 37.85 m^3/day =	1.21	1.21	1.21
Lime (LO and LSPF):	2,090 mg/L x $0.032/kg x 37.85 m^3/day =	2.43	2.43	—
Lime (LWS):	1,635 mg/L x $0.032/kg x 37.85 m^3/day =	—	—	1.90
NaHS (LWS):	260 mg/L x $0.827/kg x 37.85 m^3/day =	—	—	8.14
NaHS (LSPF):	30 mg/L x $0.827/kg x 37.85 m^3/day =	—	0.94	—
Polyelectrolyte:	0.8 mg/L x $5.62/kg x 37.85 m^3/day =	0.16	0.16	0.16
Total chemical cost per day		$4.35	$5.29	$11.96

**Maintenance: 10% of operating labor cost = $12.00 per day

††Sludge disposal: 1 m^3/month at $35/$m^3$ = $1.16 per day

‡‡Capital cost x 0.132695 = annual repayment for annuity, 8%, 12 years (11).

TABLE 13. OPERATING COSTS FOR MEDIUM-SIZED PLANT

Plant capacity = 757 m^3/day (200,000 gal/day)	Cost per day ($)				
	LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
Equipment amortization*	302.73	305.20	338.14	330.75	333.22
Operating labor†	240.00	240.00	240.00	240.00	240.00
Chemicals‡	90.96	90.96	109.74	242.66	242.66
Maintenance**	24.00	24.00	24.00	24.00	24.00
Sludge disposal††	23.20	23.20	23.20	23.20	23.20
Totals	680.89	683.36	735.08	860.61	863.08

* Equipment amortization‡‡

(LO-CL)	$798,500	x	0.132695 / 350 days	=	$302.73 per day
(LO-CLF)	805,000	x	0.132695 / 350 days	=	305.20 per day
(LSPF)	891,900	x	0.132695 / 350 days	=	338.14 per day
(LWS-CL)	872,400	x	0.132695 / 350 days	=	330.75 per day
(LWS-CLF)	878,900	x	0.132695 / 350 days	=	333.22 per day

† Operating labor: $30/hr x 8 hr/day = $240 per day

‡ Chemicals

	Cost per day ($)		
	LO-CL, LO-CLF	LSPF	LWS-CL, LWS-CLF
Sulfuric acid: 290 mg/L x $0.0507/kg x 757 m^3/day =	11.17	11.17	11.17
Sodium sulfite: 120 mg/L x $0.280/kg x 757 m^3/day =	25.54	25.54	25.54
Lime (LO and LSPF): 2,090 mg/L x $0.032/kg x 757 m^3/day =	50.83	50.83	–
Lime (LWS): 1,635 mg/L x $0.032/kg x 757 m^3/day =	–	–	39.76
NaHS (LWS): 260 mg/L x $0.827/kg x 757 m^3/day =	–	–	162.77
NaHS (LSPF): 30 mg/L x $0.827/kg x 757 m^3/day =	–	18.78	–
Polyelectrolyte: 0.8 mg/L x $5.62/kg x 757 m^3/day =	3.42	3.42	3.42
Total chemical cost per day	$ 90.96	$109.74	$242.66

** Maintenance: 10% of operating labor cost = $24.00 per day

†† Sludge disposal: 20 m^3/month at $35/$m^3$ = $23.20 per day

‡‡ Capital cost x 0.132695 = annual repayment for annuity, 8%, 12 years (11).

TABLE 14. OPERATING COSTS FOR LARGE PLANT

Plant capacity = 1,893 m^3/day (500,000 gal/day)	Cost per day ($)				
	LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
Equipment amortization*	491.43	496.54	533.36	521.64	526.76
Operating labor †	240.00	240.00	240.00	240.00	240.00
Chemicals ‡	226.19	226.19	273.16	605.70	605.70
Maintenance**	24.00	24.00	24.00	24.00	24.00
Sludge disposal††	58.00	58.00	58.00	58.00	58.00
Totals	1,039.62	1,044.73	1,128.52	1,444.69	1,450.21

* Equipment amortization ‡‡

(LO-CL)	$1,296,200	x	0.132695 / 350 days	=	$491.43 per day
(LO-CLF)	1,309,700	x	0.132695 / 350 days	=	496.54 per day
(LSPF)	1,406,800	x	0.132695 / 350 days	=	533.36 per day
(LWS-CL)	1,375,900	x	0.132695 / 350 days	=	521.64 per day
(LWS-CLF)	1,389,100	x	0.132695 / 350 days	=	526.76 per day

† Operations labor: $30/hr x 8 hr/day = $240 per day

‡ Chemicals

		Cost per day ($)		
		LO-CL, LO-CLF	LSPF	LWS-CL, LWS-CLF
Sulfuric acid:	290 mg/L x $0.0507/kg x 1,893 m^3/day =	27.79	27.79	27.79
Sodium sulfite:	120 mg/L x $0.280/kg x 1,893 m^3/day =	63.50	63.50	63.50
Lime (LO and LSPF):	2,090 mg/L x $0.032/kg x 1,893 m^3/day =	126.40	126.40	–
Lime (LWS):	1,635 mg/L x $0.032/kg x 1,893 m^3/day =	–	–	98.38
NaHS (LWS):	260 mg/L x $0.827/kg x 1,893 m^3/day =	–	–	407.03
NaHS (LSPF):	30 mg/L x $0.827/kg x 1,893 m^3/day =	–	46.97	–
Polyelectrolyte:	0.8 mg/L x $5.62 x 1,893 m^3/day =	8.50	8.50	8.50
Total chemical cost per day		$226.19	$273.16	$605.70

** Maintenance: 10% of operations labor cost = $24.00 per day

†† Sludge disposal: 50 m^3/month, $35/$m^3$ = $58.00 per day

‡‡ Capital cost x 0.132695 = annual repayment for annuity, 8%, 12 years (11)

SECTION 14

ELECTRON PHOTOMICROGRAPHS OF SLUDGES

A few of the sludges obtained from actual wastewaters and from laboratory-made dilute solutions that contain copper ions were examined at magnifications up to 50,000x. At low magnifications, the sludges invariably appeared amorphous. Only when magnifications greater than 10,000x were employed could any structure be seen. At this power, the sludges showed a granular appearance, with particles about 0.1 to 0.5 μm in diameter. No difference could be observed between sludges generated by lime alone and those generated by lime with sulfide.

The results of these exploratory photomicrographs did not suggest that further work would be particularly fruitful. Accordingly, research in this direction was discontinued.

Figure 8 shows a typical high-power (46,500x) electron photomicrograph of a lime-with-sulfide sludge.

Figure 8. Electron photomicrograph of lime-with-sulfide sludge (magnified at 46,500x).

SECTION 15

SLIDE AND CASSETTE TAPE PRESENTATION

A 35-mm color slide presentation with accompanying synchronized cassette tape narration is available on request.

The 38-slide presentation lasts about 20 min. It describes the background of sulfide precipitation of heavy metals and the purpose of the program; it contains photographs of the bench-scale equipment; it includes a condensed table of results plus the conclusions drawn from the program.

The slides are standard 35-mm, 2-in by 2-in format, and the narration is on a two-track tape cassette with sound on one channel and a 1,000-Hz slide-advance pulse on the other. Suitable equipment for viewing includes (but is not restricted to) a Kodak Ektographic projector and a Wollensak Model 2570 AV tape player.

Inquiries regarding the slide presentation should be addressed to Dr. H. B. Durham, Industrial Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

SECTION 16

CONFIDENCE LEVELS OF THE CHEMICAL ANALYSES

GENERAL

The primary objective of this program is to document the relative abilities of the five processes to remove heavy metals from wastewater, so the accuracy and reliability of the chemical analyses are of fundamental importance. Accordingly, considerable time and effort were devoted to testing the reproducibility of the results obtained by chemical analysis.

ANALYSIS OF EPA STANDARDS

Two solutions of composition known only to the EPA were supplied to test the accuracy of Boeing analyses. The results for the seven principal metals of interest to the EPA are detailed in Table 15. All Boeing analyses were within the acceptance limits designated by the EPA.

STATISTICAL REPEATABILITY TESTS

Two 12L samples of a treated wastewater (Run 5, LO-CL and LO-CLF) were analyzed three times over (on three separate days) by the two atomic absorption methods, flame and flameless, to give a total of six analyses for each of the five heavy metals tested in this study. Tables 16 and 17 show the results.

Table 18 gives the calculated limits within which the true concentrations would be expected to fall, with a 90-percent confidence level, for 99 percent of a series of estimations, based on 8.97 standard deviations (13).

The remaining conclusions drawn from the repeatability tests are that:

a. A statistically significant reduction exists at the 0.975 confidence level in the filtered, compared with the unfiltered, samples;
b. A significant difference exists at the 0.95 confidence level between the flame and flameless methods so that, in order to compare metal levels, the same method should be used for both metals being estimated.

TABLE 15. ANALYSIS OF EPA STANDARDS

Metal	Solution 1 (μg/L) Boeing analysis	EPA actual	EPA acceptance limits	Solution 2 (μg/L) Boeing analysis	EPA actual	EPA acceptance limits
Cd	12	10	2.84 to 18.0	65	70	47.5 to 85.8
Cr	79	60	21.2 to 93.6	237	250	102 to 368
Cu	55	40	4.53 to 85.3	334	350	267 to 415
Hg	1.5	3.0	0 to 7.19	2.0	8.0	0 to 17.6
Ni	107	70	21.4 to 119	279	300	161 to 452
Pb	79	80	30.3 to 132	381	400	185 to 608
Zn	71	60	23.8 to 105	388	400	206 to 612

TABLE 16. EFFLUENT FROM LO-CL PROCESS

Metal	Flame method (μg/L) 1	2	3	Mean	SD*	Flameless method (μg/L) 1	2	3	Mean	SD*
Copper	10.8	11.4	10.7	11.0	0.4	11.6	13.4	11.8	12.3	1.0
Chromium	15.5	16.7	14.3	15.5	1.2	21.6	19.3	20.5	20.5	1.2
Nickel	135	143	137	138	4.2	114	111	109	111	2.5
Cadmium	3.2	3.7	4.3	3.7	0.55	3.0	2.9	2.9	2.9	0.06
Zinc	41	48	25	38	11.8	6.9	6.1	4.2	5.7	1.4

*Standard deviation

TABLE 17. EFFLUENT FROM LO-CLF PROCESS

Metal	Flame method (μg/L) 1	2	3	Mean	SD*	Flameless method (μg/L) 1	2	3	Mean	SD*
Copper	7.2	6.2	7.3	6.9	0.61	10.2	6.6	7.7	8.2	1.8
Chromium	10.3	10.3	10.6	10.4	0.17	13.3	12.7	12.2	12.7	0.55
Nickel	103.4	104.6	106	104.7	1.3	100	96	92	96	4.0
Cadmium	< 1	< 1	< 1	< 1	–	<0.3	<0.3	<0.3	<0.3	–
Zinc	1.9	1.6	4.2	2.6	1.4	1.3	1.7	1.3	1.4	0.2

*Standard deviation

TABLE 18. CONFIDENCE LEVELS OF THE ANALYSES

Metal	Flame method LO-CL	LO-CLF	Flameless method LO-CL	LO-CLF
Copper	±33%	±79%	±73%	±197%
Chromium	±69%	±15%	±53%	±39%
Nickel	±27%	±11%	±20%	±37%
Cadmium	±133%	–	±19%	–
Zinc	±279%	±483%	±220%	±128%

SECTION 17

CONSULTANT'S REPORT

Consultant: Dr. D. Bhattacharyya
Department of Chemical Engineering, University of Kentucky

Industries engaged in metal finishing or metal production operations use large quantities of contact process water, and the spent process wastewater (rinse water) streams contain heavy metals, such as Cu, Cd, Pb, Zn, Ni, Cr, Sn, Ag, and cyanides. Although hydroxide (lime) precipitation of heavy metals, followed by settling, is the process that is used most often to treat industrial wastewaters, the amphoteric nature of some precipitates [$M(OH)_2$ (ppt) + $OH^- \rightleftharpoons M(OH)_3^-$], settling problems, and the presence of complexing agents may reduce metal removal efficiency. With sulfide precipitation, the high reactivity of sulfides ($S^=$, HS^-, H_2S) with heavy metal ions and the very low solubility of heavy metal sulfides over a broad pH range are attractive features when this process is compared to the corresponding hydroxide precipitation process. The optimum sulfide dosage and pH adjustments depend, of course, on the wastewater characteristics.

Although heavy metals can be precipitated with soluble sulfide salts (Na_2S or NaHS) or with sparingly soluble metal sulfides (such as FeS), the use of FeS often requires higher than stoichiometric dosages. The Boeing Company conducted extensive experimental investigation of the soluble sulfide process and lime precipitation process with various industrial metal finishing (anodizing, metal cleaning, printed circuit etching, and several types of electroplating) wastewaters.

A side-by-side comparison of continuous-flow sulfide precipitation and hydroxide precipitation processes has not been reported previously in the literature. Sulfide precipitation experiments were conducted in the pH 8.0 to 9.0 range. Lime precipitation with settling followed by sulfide precipitation and filtration (LSPF process) and a combined lime-sulfide-settling-filtration (LWS-CLF) process were consistently better than the hydroxide processes. In several cases (moderate Zn and Cu concentration in the influent), lime precipitation-settling followed by filtration (to remove fine precipitates) was also highly effective in removing heavy metals from the wastewaters. The precipitation results also indicated that with several wastes (higher concentrations), the lime precipitation process produced sludge volumes 1.3 to 1.9 times higher than the LWS (sulfide) process.

Sulfide precipitation was considerably better than the lime precipitation process for waste number 12, which contained a high concentration of Zn (440 mg/L), in the presence of ammonium ion, and for waste number 9, which contained 24 mg/L Cu and 99 mg/L Ni at a high pH of 11.4 (high pH may indicate presence of complexing agents). Table 19 shows the Zn removals (waste No. 12) obtained with various precipitation processes. With waste number 9, both Cu and Ni removals are considerably better with the sulfide processes, as shown in Table 20.

TABLE 19. ZINC REMOVAL FROM WASTE NO. 12

pH	Zinc removal (%)				
	LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
8.5	83.0	84.1	89.9	99.4	99.0
9.0	91.5	93.4	99.5	99.8	–

TABLE 20. METAL REMOVAL FROM WASTE NO. 9

Metal	pH	Metal removal (%)				
		LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
Copper	8.8	58.3	66.7	99.7	89.2	98.3
Nickel	8.8	83.5	87.8	98.8	92.9	95.8

For all the wastewaters studied, although LSPF and LWS-CLF gave similar effluent quality, the sulfide polishing (LSPF) process would be preferred on the basis of considerably lower sulfide dosage (thus lower sulfide chemical cost) requirements. With the LSPF process, two separate reaction stages would be required. The total operating costs (NaHS as sulfide) with the LSPF process would be 5 to 9 percent higher than the conventional lime precipitation process.

Although the sulfide precipitation studies conducted at Boeing were at pH 8 to 9, the sulfide precipitation of heavy metals is highly effective even at lower pH values. Among the heavy metals, HgS has the lowest solubility, and ZnS and NiS have the highest solubility. The precipitates' solubility sequence is $HgS < CuS < CdS < PbS < ZnS < NiS$. Hg, Cu, Cd, and Pb can be precipitated with sulfide (Na_2S or NaHS) even at pH 3 without any H_2S gas formation. Effective precipitation of Zn and Ni occurs at pH $\geq$ 6. Sulfide precipitation is quite effective, even in the acidic pH; thus, selective metal recovery and the obtaining of effluent water of low calcium content (for possible water recycling because no lime may be required) are possible.

A full-scale sulfide precipitation process (Na_2S as sulfide source) with a capacity of 1.0×10^6 gallons per day is operating at Boliden Metall Corporation of Sweden to treat smelter (Cu, Pb, Zn smelting) wastewaters. One copper smelter in Japan has a sulfide precipitation process to recover heavy metals as sulfides. A New Hampshire aluminum company operates a chrome removal treatment system with $FeCl_3$ and Na_2S to remove both hexavalent and trivalent Cr. The Permutit Company and Holley Carburetor Division of Colt Industries demonstrated the use of the sulfide process (Sulfex process uses freshly prepared FeS by reacting NaHS with $FeSO_4$) at Paris, Tennessee, and obtained effluent waters containing Cr and Zn at less than a 0.05-mg/L level. An extensive bench-scale study involving lime-sulfide precipitation of heavy metals and arsenic from smelter (Cu) wastewaters is also in progress at the University of Kentucky.

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APPENDIX A

CASE HISTORY DATA OF 16 TEST RUNS

The test runs are arranged in this appendix in the order of increasing electrical conductivity of the raw feed. Each case history includes data on the wastewater sample raw feed analysis, processed effluent analysis, process consumables, and sludge volume.

The data were generated from 14 wastewater samples that represented nonferrous metal smelting, electroplating, anodizing, cleaning, and etching operations. Samples came from industrial plant sources across the United States. Each wastewater sample was used in a test run at a pH value selected as an optimum for precipitation of its heavy metals. Two samples were tested at a second pH value where doubt existed as to the true optimum pH value.

TEST RUN 1

Description of wastewater: Rinse from copper printed circuit etching and copper deposition (electrolytic and electroless)

Source area: Seattle, Washington

Treatment process details*

Precipitation pH for lime-only and lime-with-sulfide processes	Sludge volume†	Process consumables (mg/L)	
8.5	LO: < 2	H_2SO_4 for Cr^{6+} reduction:	120
		Na_2SO_3 for Cr^{6+} reduction:	31
		CaO for LO process:	86
	LWS: < 2	S for LWS process:	18
		S for LSPF process:	3.5

Chemical analysis (all values except conductivity and pH in μg/L)

Measurement	Before–raw feed	Value after treatment by process of*:				
		LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
Cd	8	2	<<1	<<1	1	<<1
Cr (total)	215	203	3	2	215	6
Cu	2.3×10^3	1.8×10^3	200	67	1.9×10^3	5
Ni	209	217	86	77	209	88
Zn	770	430	53	14	424	13
pH	5.2					
Conductivity‡	115					
Color	colorless					
Cr^{6+}	73					
Hg	<1					
Pb	192	185	17	15	192	13
Ag	<3	1	1	1	1	1
Sn	3.3×10^3	308	139	348	432	279

* Process code: LO = lime only; LSPF = lime, sulfide polished and filtered; LWS = lime with sulfide; CL = clarified; CLF = clarified and filtered

† Volume per volume, percentage after 1 hr settling

‡ μmho/cm at 18.5°C

TEST RUN 2

Description of wastewater: Rinse from electroplating

Source area: Portland, Oregon

Treatment process details*

Precipitation pH for lime-only and lime-with-sulfide processes	Sludge volume †	Process consumables (mg/L)	
8.5	LO: < 2	H_2SO_4 for Cr^{6+} reduction:	264
		Na_2SO_3 for Cr^{6+} reduction:	132
		CaO for LO process:	132
	LWS: < 2	S for LWS process:	1
		S for LSPF process:	1

Chemical analysis (all values except conductivity and pH in μg/L)

Measurement	Before—raw feed	Value after treatment by process of*:				
		LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
Cd	268	179	22	23	139	19
Cr (total)	949	459	15	29	484	57
Cu	87	59	24	14	36	8
Ni	19	18	18	8	16	7
Zn	112	100	20	10	78	10
pH	8.0					
Conductivity ‡	217					
Color	colorless					
Cr^{6+}	396					
Fe	408	56	12	20	150	21
Hg	<1					

*Process code: LO = lime only; LSPF = lime, sulfide polished and filtered; LWS = lime with sulfide; CL = clarified; CLF = clarified and filtered

† Volume per volume, percentage after 1 hr settling

‡ μmho/cm at 17°C

TEST RUN 3

Description of wastewater: Rinse from electroplating and metal finishing by carburetor manufacturer

Source area: Warren, Michigan

Treatment process details*

Precipitation pH for lime-only and lime-with-sulfide processes	Sludge volume †	Process consumables (mg/L)	
8.75	LO: 24	H_2SO_4 for Cr^{6+} reduction:	370
		Na_2SO_3 for Cr^{6+} reduction:	610
		CaO for LO process:	290
	LWS: 19	S for LWS process:	43
		S for LSPF process:	25

Chemical analysis (all values except conductivity and pH in μg/L)

Measurement	Before—raw feed	Value after treatment by process of*:				
		LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
Cd	4					
Cr (total)	200×10^3	1,060	76	56	437	58
Cu	30	22	22	14	7	5
Ni	106	10	17	8	4	4
Zn	90×10^3	1,000	210	10	490	15
pH	4.5					
Conductivity ‡	550					
Color	yellow					
Cr^{6+}	91×10^3					
Hg	<1					
Pb	<25					
Ag	20					
Sn	1.2×10^3	<2	<2	<2	<2	<2

*Process code: LO = lime only; LSPF = lime, sulfide polished and filtered; LWS = lime with sulfide; CL = clarified; CLF = clarified and filtered

† Volume per volume, percentage after 1 h settling

‡ μmho/cm at 18.5°C

TEST RUN 4

Description of wastewater: Rinse from anodizing and electroplating

Source area: Minneapolis, Minnesota

Treatment process details*

Precipitation pH for lime-only and lime-with-sulfide processes	Sludge volume †	Process consumables (mg/L)	
9.0	LO: <4	H_2SO_4 for Cr^{6+} reduction:	140
		Na_2SO_3 for Cr^{6+} reduction:	200
	LWS: <4	CaO for LO process:	20
		S for LWS process:	1
		S for LSPF process:	0.5

Chemical analysis (all values except conductivity and pH in μg/L)

Measurement	Before—raw feed	Value after treatment by process of*:				
		LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
Cd	400	98	11	16	55	29
Cr (total)	12.6×10^3	2,200	178	237	957	470
Cu	800	69	20	18	40	24
Ni	3.2×10^3	467	69	102	350	197
Zn	11×10^3	2,145	167	331	1,200	560
pH	7.05					
Conductivity‡	700					
Color	pale yellow					
Cr^{6+}	10.4×10^3	<5		<5	<5	
Pb	17	12	<2	<2	6	3
Ag	29	3	3	3	3	3
Sn	350	215	155	185	169	213

* Process code: LO = lime only; LSPF = lime, sulfide polished and filtered; LWS = lime with sulfide; CL = clarified; CLF = clarified and filtered

† Volume per volume, percentage after 1 hr settling

‡ μmho/cm at 21°C

TEST RUN 5

Description of wastewater: Rinse from anodizing and electroplating

Source area: Lincoln, Nebraska

Treatment process details*

Precipitation pH for lime-only and lime-with-sulfide processes	Sludge volume †	Process consumables (mg/L)	
10.5	LO: 6	H_2SO_4 for Cr^{6+} reduction:	0
		Na_2SO_3 for Cr^{6+} reduction:	0
	LWS: 4	CaO for LO process:	98
		S for LWS process:	19
		S for LSPF process:	14

Chemical analysis (all values except conductivity and pH in μg/L)

Measurement	Before—raw feed	Valu after treatment by process of*:				
		LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
Cd	9	3	<3	<3	<3	<3
Cr (total)	18	18	12	14	9	13
Cu	24	12	8	6	4	5
Ni	789	125	100	100	69	111
Zn	33	6	3	3	5	5
pH	7.1					
Conductivity‡	1,320					
Color	colorless					
Hg	<10					
Pb	211	1	1			
Ag	600	2	2	3	2	2
Sn	280	40	36	131	103	228
CN	1×10^3					

*Process code: LO = lime only; LSPF = lime, sulfide polished and filtered; LWS = lime with sulfide; CL = clarified; CLF = clarified and filtered

† Volume per volume, percentage after 1 hr settling

‡ μmho/cm at 22°C

TEST RUN 6

Description of wastewater: **Rinse from electroplating**

Source area: **Cleveland, Ohio**

Treatment process details*

Precipitation pH for lime-only and lime-with-sulfide processes	Sludge volume †	Process consumables (mg/L)	
8.5	LO: 5 LWS: 6	H_2SO4 for Cr^{6+} reduction:	339
		Na_2SO_3 for Cr^{6+} reduction:	25
		CaO for LO process:	145
		S for LWS process:	91
		S for LSPF process:	67

Chemical analysis (all values except conductivity and pH in μg/L)

Measurement	Before—raw feed	Value after treatment by process of*:				
		LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
Cd	<40	<1	<1	<1	<1	<1
Cr (total)	1.7×10^3	109	39	20	187	17
Cu	21×10^3	1,300	367	11	2,250	169
Ni	119×10^3	12×10^3	9.4×10^3	5.3×10^3	11×10^3	3.5×10^3
Zn	13×10^3	625	10	5	192	8
pH	7.1					
Conductivity‡	1,500					
Color	pale green					
Fe		2	<2	<2	5	<2
Pb	13	7	5	3	4	3
Ag	6					

*Process code: LO = lime only; LSPF = lime, sulfide polished and filtered; LWS = lime with sulfide; CL = clarified; CLF = clarified and filtered

† Volume per volume, percentage after 1 hr settling

‡ μmhc/cm at 21°C

TEST RUN 7

Description of wastewater: Rinse from anodizing and electroplating

Source area: Kent, Washington

Treatment process details*

Precipitation pH for lime-only and lime-with-sulfide processes	Sludge volume †	Process consumables (mg/L)	
9.25	LO: 14 LWS: 14	H_2SO_4 for Cr^{6+} reduction:	972
		Na_2SO_3 for Cr^{6+} reduction:	211
		CaO for LO process:	389
		S for LWS process:	1
		S for LSPF process:	1

Chemical analysis (all values except conductivity and pH in μg/L)

Measurement	Before–raw feed	Value after treatment by process of*:				
		LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
Cd	76	27	16	22	25	20
Cr (total)	8.5×10^3	318	65	139	295	239
Cu	1.3×10^3	244	236	143	212	166
Ni	944	80	49	49	349	250
Zn	131	46	42	40	35	24
pH	10.6					
Conductivity‡	4,400					
Color	yellow					
Hg	<10					
Pb	45	15	14	43	23	13
Ag	44	19	11	9	9	8
Sn	460	<10	<10	<10	<10	<10

*Process code: LO = lime only; LSPF = lime, sulfide polished and filtered; LWS = lime with sulfide; CL = clarified; CLF = clarified and filtered

† Volume per volume, percentage after 1 hr settling

‡ μmho/cm at 22°C

TEST RUN 8

Description of wastewater: From a nonferrous metal smelter settling pond fed by water from a flue gas zinc extractor and by scrubber water from copper-phosphorus process

Source area: Perth Amboy, New Jersey

Treatment process details*

Precipitation pH for lime-only and lime-with-sulfide processes	Sludge volume †	Process consumables (mg/L)	
8.5	LO: 41	H_2SO_4 for Cr^{6+} reduction:	0
		Na_2SO_3 for Cr^{6+} reduction:	0
		CaO for LO process:	1,004
	LWS: 29	S for LWS process:	60
		S for LSPF process:	4

Chemical analysis (all values except conductivity and pH in μg/L)

Measurement	Before—raw feed	Value after treatment by process of*:				
		LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
Cd	15×10^3	80	7	4	50	2
Cr (total)	100	100	23	5	3	2
Cu	7×10^3	39	0.14	14	38	6
Ni	123	40	26	106	108	115
Zn	114×10^3	511	30	36	309	15
pH	2.2					
Conductivity ‡	4,700					
Color	colorless					
As	1.4×10^3	54	38	40	44	49
Cr^{6+}	<4					
Hg	<1					
Pb	5×10^3	38	3	3	27	2
Ag	1					
Sn	5×10^3					
Se	$<1 \times 10^3$	44	40	36	44	44

*Process code: LO = lime only; LSPF = lime, sulfide polished and filtered; LWS = lime with sulfide; CL = clarified; CLF = clarified and filtered

† Volume per volume, percentage after 1 hr settling

‡ μmho/cm at 19°C

TEST RUN 9

Description of wastewater: Rinse from electroplating

Source area: Los Angeles, California

Treatment process details*

Precipitation pH for lime-only and lime-with-sulfide processes	Sludge volume†	Process consumables (mg/L)	
8.75	LO: <2	H_2SO_4 for Cr^{6+} reduction:	2,420
		Na_2SO_3 for Cr^{6+} reduction:	97
		CaO for LO process:	515
	LWS: <2	S for LWS process:	190
		S for LSPF process:	65

Chemical analysis (all values except conductivity and pH in μg/L)

Measurement	Before—raw feed	Value after treatment by process of*:				
		LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
Cd	<100	97	71	3	12	8
Cr (total)	310	40	25	33	90	48
Cu	24×10^3	10×10^3	8×10^3	73	2.6×10^3	400
Ni	99×10^3	16×10^3	12×10^3	1.2×10^3	7.0×10^3	4.2×10^3
Zn	253×10^3	400	295	8	567	9
pH	11.4					
Conductivity‡	5,500					
Color	yellow					
Hg	<0.1					
Ag	4					
CN	31×10^3					

*Process code: LO = lime only; LSPF = lime, sulfide polished and filtered; LWS = lime with sulfide; CL = clarified; CLF = clarified and filtered

† Volume per volume, percentage after 1 hr settling

‡ μmho/cm at 19°C

TEST RUN 10

Description of wastewater: Rinse from electroplating

Source area: Chicago, Illinois

Treatment process details*

Precipitation pH for lime-only and lime-with-sulfide processes	Sludge volume†	Process consumables (mg/L)	
10.0	LO: 43 LWS: 37	H_2SO_4 for Cr^{6+} reduction:	0
		Na_2SO_3 for Cr^{6+} reduction:	41
		CaO for LO process:	2,680
		S for LWS process:	400
		S for LSPF process:	141

Chemical analysis (all values except conductivity and pH in μg/L)

Measurement	Before—raw feed	Value after treatment by process of*:				
		LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
Cd	58×10^3	1,130	923	<10	26	<10
Cr (total)	5×10^3	138	103	37	49	50
Cu	2×10^3	909	943	929	60	160
Ni	3×10^3	2.2×10^3	2.3×10^3	2.6×10^3	1.8×10^3	1.9×10^3
Zn	290×10^3	1.2×10^3	510	12	216	38
pH	2.4					
Conductivity‡	5,600					
Color	colorless					
Fe	740×10^3	2×10^3	334	305	563	229
Hg	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Ag	14	14	10	8	7	7
Sn	5×10^3	129	81	71	71	71

*Process code: LO = lime only; LSPF = lime, sulfide polished and filtered; LWS = lime with sulfide; CL = clarified; CLF = clarified and filtered

† Volume per volume, percentage after 1 hr settling

‡ μmho/cm at 19°C

TEST RUN 11

Description of wastewater: Rinse from aluminum cleaning, anodizing, and electroplating

Source area: Auburn, Washington

Treatment process details*

Precipitation pH for lime-only and lime-with-sulfide processes	Sludge volume †	Process consumables (mg/L)	
8.5	LO: 18	H_2SO4 for Cr^{6+} reduction:	0
		Na_2SO_3 for Cr^{6+} reduction:	226
		CaO for LO process:	1,530
	LWS: 16	S for LWS process:	8
		S for LSPF process:	1

Chemical analysis (all values except conductivity and pH in μg/L)

Measurement	Before—raw feed	Value after treatment by process of*:				
		LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
Cd	45	15	8	20	11	7
Cr (total)	163×10^3	3,660	250	159	1,660	68
Cu	4.7×10^3	135	0.33	3	82	18
Ni	185	30	38	18	33	31
Zn	2.8×10^3	44	10	11	26	2
pH	1.7					
Conductivity ‡	10,600					
Color	yellow					
Pb	119	119	88	120	104	59

*Process code: LO = lime only; LSPF = lime, sulfide polished and filtered; LWS = lime with sulfide; CL = clarified; CLF = clarified and filtered

† Volume per volume, percentage after 1 hr settling

‡ μmho/cm at 22°C

TEST RUN 12*

Description of wastewater: Rinse from electroplating

Source area: Chicago, Illinois

Treatment process details†

Precipitation pH for lime-only and lime-with-sulfide processes	Sludge volume‡	Process consumables (mg/L)	
8.5	LO: 20	H_2SO_4 for Cr^{6+} reduction:	0
		Na_2SO_3 for Cr^{6+} reduction:	0
	LWS: 10	CaO for LO process:	760
	LSPF: 2	S for LWS process:	260
		S for LSPF process:	108

Chemical analysis (all values except conductivity and pH in μg/L)

Measurement	Before—raw feed	Value after treatment by process of†:				
		LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
Cd	34	20	20	1	1	1
Cr (total)	3					
Cu	20	8	0.8	3	1	1
Ni	64	42	42	42	34	50
Zn	440×10^3	75×10^3	71×10^3	4.7×10^3	2.5×10^3	4.6×10^3
pH	6.4					
Conductivity**	12,100					
Color	colorless					
Hg	<10					
Pb	45	15	17	17	22	15
Ag	61	4	4	5	5	5
Sn	200	<10	<10	<10	<10	<10
NH_4	††					

* Test runs 12 and 13 were made with the same raw feed wastewater: run 12 at pH = 8.5 and run 13 at pH = 9.0

† Process code: LO = lime only; LSPF = lime, sulfide polished and filtered; LWS = lime with sulfide; CL = clarified; CLF = clarified and filtered

‡ Volume per volume, percentage after 1 hr settling

** μmho/cm at 25°C

†† Qualitative tests indicated the presence of significant amounts of ammonium

TEST RUN 13*

Description of wastewater: Rinse from electroplating

Source area: Chicago, Illinois

Treatment process details†

Precipitation pH for lime-only and lime-with-sulfide processes	Sludge volume ‡		Process consumables (mg/L)	
9.0	LO:	–	H_2SO4 for Cr^{6+} reduction:	0
			Na_2SO_3 for Cr^{6+} reduction:	0
			CaO for LO process:	911
	LWS:	–	S for LWS process:	–
			S for LSPF process:	–

Chemical analysis (all values except conductivity and pH in μg/L)

Measurement	Before–raw feed	Value after treatment by process of †:				
		LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
Cd	34	21	21	1	1	1
Cr (total)	3					
Cu	20	7	8	4	2	1
Ni	64	29	29	31	72	34
Zn	440×10^3	37×10^3	29×10^3	2×10^3	730	600
pH	6.4					
Conductivity**	12,100					
Color	colorless					
Hg	<10					
Pb	45	13	14	13	9	11
Ag	61	4	4	4	1	3
Sn	200	<10	<10	<10	<10	<10
NH_4	††					

* Test runs 12 and 13 were made with the same raw feed wastewater: run 12 at pH = 8.5 and run 13 at pH = 9.0

† Process code: LO = lime only; LSPF = lime, sulfide polished and filtered; LWS = lime with sulfide; CL = clarified; CLF = clarified and filtered

‡ Volume per volume, percentage after 1 hr settling

** μmho/cm at 25°C

†† Qualitative tests indicated the presence of significant amounts of ammonium

TEST RUN 14*

Description of wastewater: Rinse from electroplating

Source area: Atlanta, Georgia

Treatment process details †

Precipitation pH for lime-only and lime-with-sulfide processes	Sludge volume‡	Process consumables (mg/L)	
8.5	LO: 59	H_2SO_4 for Cr^{6+} reduction:	0
		Na_2SO_3 for Cr^{6+} reduction:	156
		CaO for LO process:	5,009
	LWS: 53	S for LWS process:	995
		S for LSPF process:	16

Chemical analysis (all values except conductivity and pH in μg/L)

Measurement	Before—raw feed	Value after treatment by process of †:				
		LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
Cd	1.4×10^3	432	360	70		
Cr (total)	10.3×10^3	34	5	9		
Cu	900	28	28	7		
Ni	35×10^3	1,000	750	96		
Zn	930×10^3	9.6×10^3	1.4×10^3	340		
pH	1.2				No tests run. The extremely high sulfide demand would make a full-scale process uneconomical.	
Conductivity**	75,000					
Color	brown					
Fe	415×10^3	19×10^3	1.5×10^3	1.5×10^3		
Hg	1					
Pb	500	16	17	16		
Ag	64	<2	<2	<2		

* Test runs 14 and 15 were made with the same raw feed wastewater: run 14 at pH = 8.5 and run 15 at pH = 10.0

† Process code: LO = lime only; LSPF = lime, sulfide polished and filtered; LWS = lime with sulfide; CL = clarified; CLF = clarified and filtered

‡ Volume per volume, percentage after 1 hr settling

** μmho/cm at 23°C

TEST RUN 15 *

Description of wastewater: Rinse from electroplating

Source area: Atlanta, Georgia

Treatment process details †

Precipitation pH for lime-only and lime-with-sulfide processes	Sludge volume ‡	Process consumables (mg/L)	
10.0	LO: 62 LWS: 46	H_2SO_4 for Cr^{6+} reduction:	0
		Na_2SO_3 for Cr^{6+} reduction:	156
		CaO for LO process:	5,428
		S for LWS process:	1,400
		S for LSPF process:	8

Chemical analysis (all values except conductivity and pH in μg/L)

Measurement	Before–raw feed	Value after treatment by process of †:				
		LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
Cd	1.4×10^3	73	66			
Cr (total)	10.3×10^3	19	22			
Cu	900	10	8			
Ni	35×10^3	35	21			
Zn	930×10^3	3.3×10^3	1.0×10^3			
pH	1.2				No tests run. The extremely high sulfide demand would make a full-scale process uneconomical.	
Conductivity**	75,000					
Color	brown					
Fe	415×10^3	2.0×10^3	1.6×10^3			
Hg	1					
Pb	500	17	15			
Ag	64	<2	<2			

*Test runs 14 and 15 were made with the same raw feed wastewater: run 14 at pH = 8.5 and run 15 at pH = 10.0

†Process code: LO = lime only; LSPF = lime, sulfide polished and filtered; LWS = lime with sulfide; CL = clarified; CLF = clarified and filtered

‡Volume per volume, percentage after 1 hr settling

**μmho/cm at 23°C

TEST RUN 16

Description of wastewater: Rinse from electroplating

Source area: Glendale, California

Treatment process details*

Precipitation pH for lime-only and lime-with-sulfide processes	Sludge volume †		Process consumables (mg/L)	
1st stage‡: 6.2		78	H_2SO_4 for Cr^{6+} reduction:	0
			Na_2SO_3 for Cr^{6+} reduction:	31
2d stage‡: 9.0	LO:	23	CaO for LO process:	14,380
			S for LWS process:	381
	LWS:	13	S for LSPF process:	5

Chemical analysis (all values except conductivity and pH in μg/L)

Measurement	Before—raw feed	Value after treatment by process of*:				
		LO-CL	LO-CLF	LSPF	LWS-CL	LWS-CLF
Cd	58	7	12	<5	<5	<5
Cr (total)	6.3×10^3	4	2	3	5	7
Cu	1.1×10^3	860	848	132	13	13
Ni	160	30	34	34	33	23
Zn	650×10^3	2.8×10^3	2.3×10^3	242	104	19
pH	1.2					
Conductivity**	149,000					
Color	colorless					
Cr^{6+}	<5	<1	<1	<1	<1	<1
Hg	<1					
Ag	16					

*Process code: LO = lime only; LSPF = lime, sulfide polished and filtered; LWS = lime with sulfide; CL = clarified; CLF = clarified and filtered

†Volume per volume, percentage after 1 hr settling

‡Because of the exceptionally large volume of sludge generated by this wastewater, precipitation was carried out in two stages

**μmho/cm at 20°C

APPENDIX B

ANALYTICAL METHODS

Chemical analyses were made for the following elements, compounds, and values using the following methods:

a. Arsenic and selenium—Furnace atomic absorption spectroscopy, Some Applications of the IL 751 Atomic Absorption Spectrophotometer, Engineering and Applications Staff, Instrumentation Laboratory Inc., Wilmington, Maine 01887

b. Cadmium, total chromium, copper, nickel, zinc, lead, silver, tin, iron:

   1. For levels >50 μg/L: Flame atomic absorption method on samples concentrated by boiling, Methods for Chemical Analysis of Water and Waste, U.S. Environmental Protection Agency

   2. For levels <50 μg/L: Flameless atomic absorption method, Instrumentation Laboratory Inc., Analytical Instrument Division, Jonspin Road, Wilmington, Maine 01887

c. Conductivity—Conductivity meter, YSI Model 33 S-C-T, Yellow Springs Instrument Co. Inc., Yellow Springs, Ohio 45387

d. Cyanide—Measurement by specific ion electrode, Orion Research Analytical Methods Guide, 7th Edition, May 1975

e. Hexavalent chromium—Diphenylcarbazide colorimetric procedure, Standard Methods, 13th Edition, p. 426

f. Mercury—Manual cold vapor technique, Methods for Chemical Analysis of Water and Waste, U.S. Environmental Protection Agency

g. Sludge volume determination—Visual measurement of treated sample in graduated cylinder after 1 hour settling. Sludge volumes are expressed in terms of the volume occupied by the sludge as a percentage of the total volume treated.

APPENDIX C

COMPARISON PLOTS OF FIVE METAL CONCENTRATIONS FOR ALL SAMPLES

The comparison plots show results from five processes using cadmium, copper, chromium, nickel, and zinc effluent metal concentrations for all wastewater samples.

Each point plotted in the diagrams has two coordinates: the concentration of a metal in the process A effluent (x-axis) and the concentration of the same metal in the process B effluent (y-axis). A point below the 45-deg line results when there is a higher concentration of the metal in process A effluent; if all the points are below the line, process A is clearly less effective in removing that metal than process B. For example, the copper diagram in Figure C-1 shows that the LO-CL process is less effective in removing copper than the LSPF process for all 14 wastewaters except one. The cadmium diagram in Figure C-1 shows no obvious advantage for either the LO-CL or LSPF process for removing cadmium.

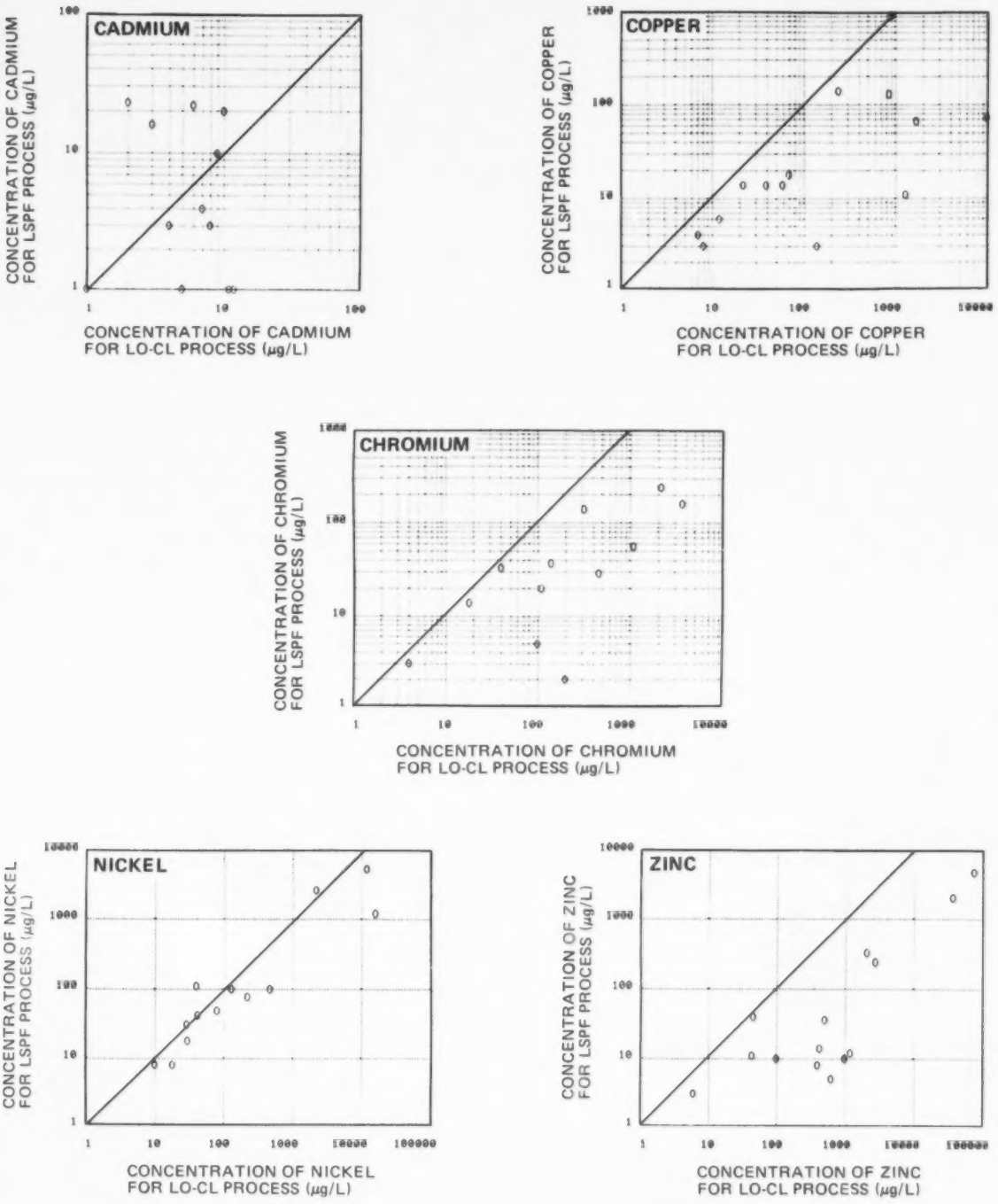
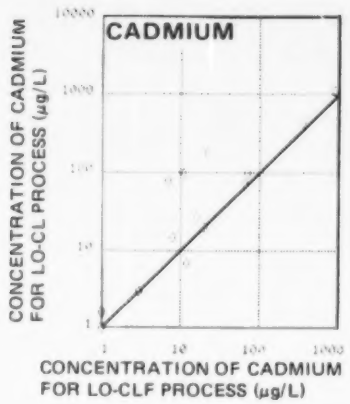
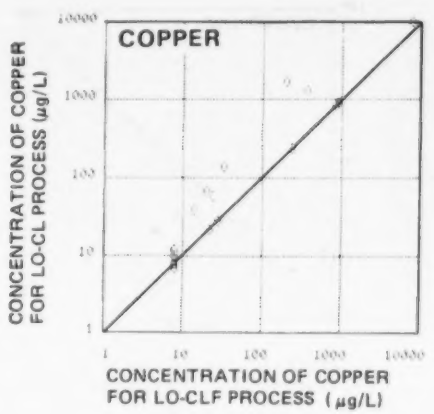
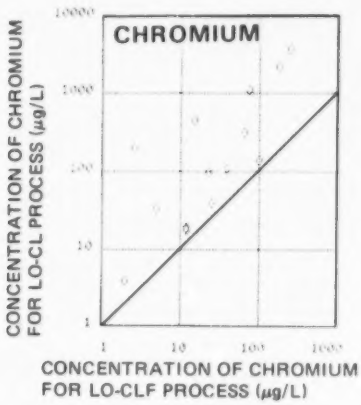
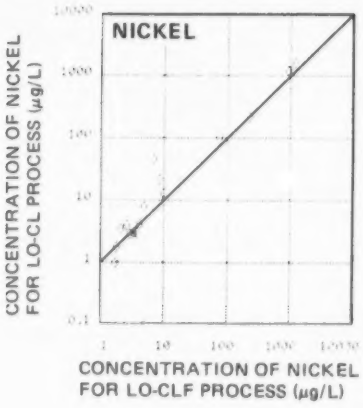

CADMIUM
CONCENTRATION OF CADMIUM FOR LSPF PROCESS (µg/L)
CONCENTRATION OF CADMIUM FOR LO-CL PROCESS (µg/L)
COPPER
CONCENTRATION OF COPPER FOR LSPF PROCESS (µg/L)
CONCENTRATION OF COPPER FOR LO-CL PROCESS (µg/L)
CHROMIUM
CONCENTRATION OF CHROMIUM FOR LSPF PROCESS (µg/L)
CONCENTRATION OF CHROMIUM FOR LO-CL PROCESS (µg/L)
NICKEL
CONCENTRATION OF NICKEL FOR LSPF PROCESS (µg/L)
CONCENTRATION OF NICKEL FOR LO-CL PROCESS (µg/L)
ZINC
CONCENTRATION OF ZINC FOR LSPF PROCESS (µg/L)
CONCENTRATION OF ZINC FOR LO-CL PROCESS (µg/L)

Figure C-1. Comparison of LO-CL process and LSPF process using Cd, Cu, Cr, Ni, and Zn effluent metal concentrations for all wastewater samples.









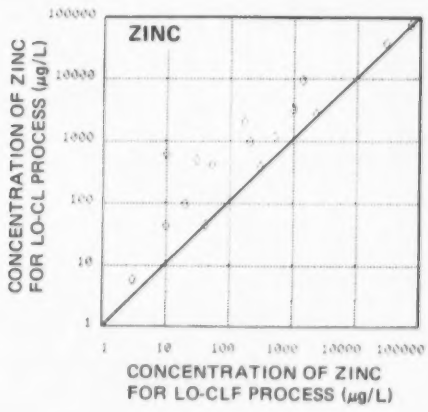


Figure C-2. Comparison of LO-CLF process and LO-CL process using Cd, Cu, Cr, Ni, and Zn effluent metal concentrations for all wastewater samples.

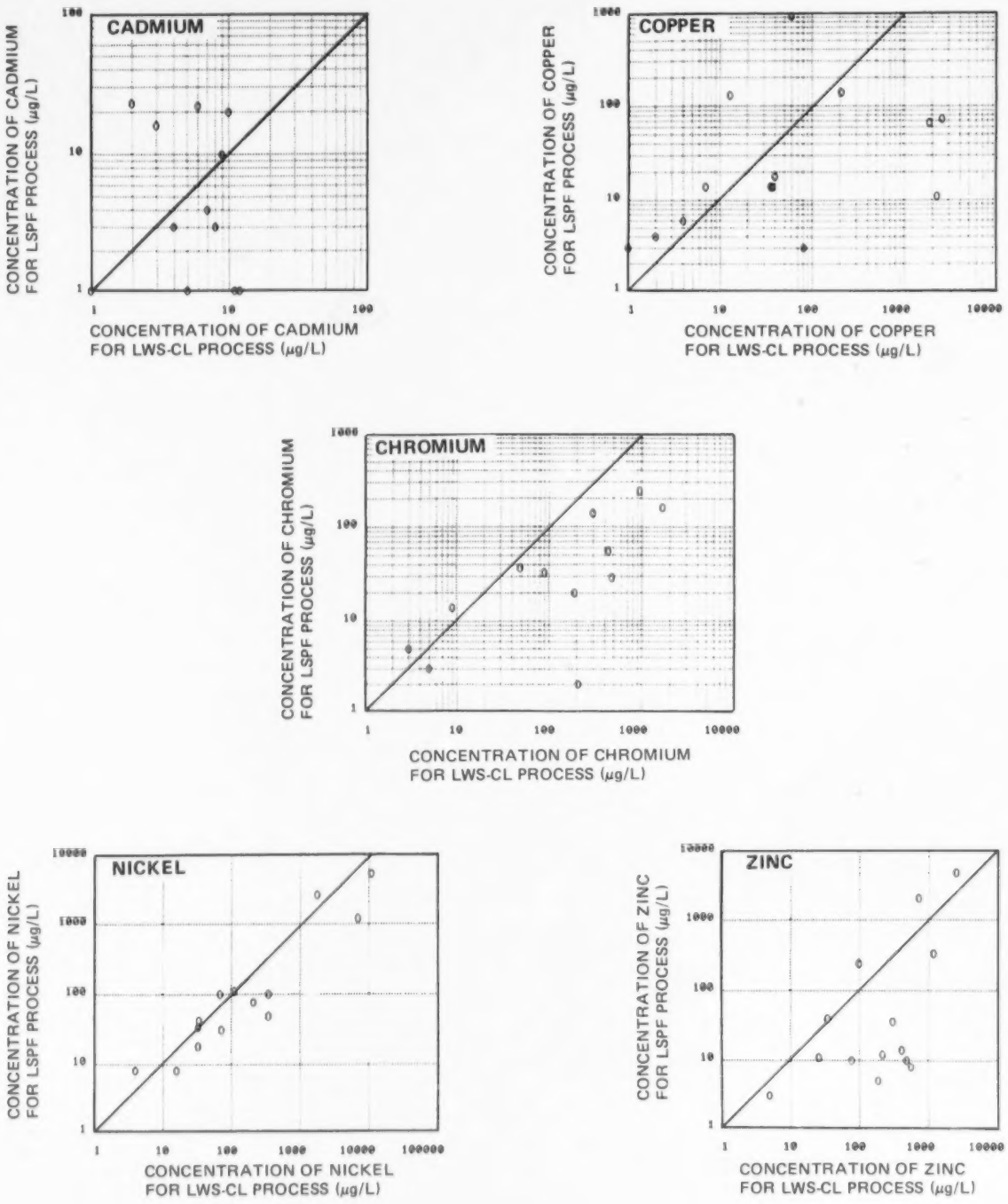

CADMIUM
CONCENTRATION OF CADMIUM FOR LSPF PROCESS (µg/L)
CONCENTRATION OF CADMIUM FOR LWS-CL PROCESS (µg/L)
COPPER
CONCENTRATION OF COPPER FOR LSPF PROCESS (µg/L)
CONCENTRATION OF COPPER FOR LWS-CL PROCESS (µg/L)
CHROMIUM
CONCENTRATION OF CHROMIUM FOR LSPF PROCESS (µg/L)
CONCENTRATION OF CHROMIUM FOR LWS-CL PROCESS (µg/L)
NICKEL
CONCENTRATION OF NICKEL FOR LSPF PROCESS (µg/L)
CONCENTRATION OF NICKEL FOR LWS-CL PROCESS (µg/L)
ZINC
CONCENTRATION OF ZINC FOR LSPF PROCESS (µg/L)
CONCENTRATION OF ZINC FOR LWS-CL PROCESS (µg/L)

Figure C-3. Comparison of LSPF process and LWS-CL process using Cd, Cu, Cr, Ni, and Zn effluent metal concentrations for all wastewater samples.

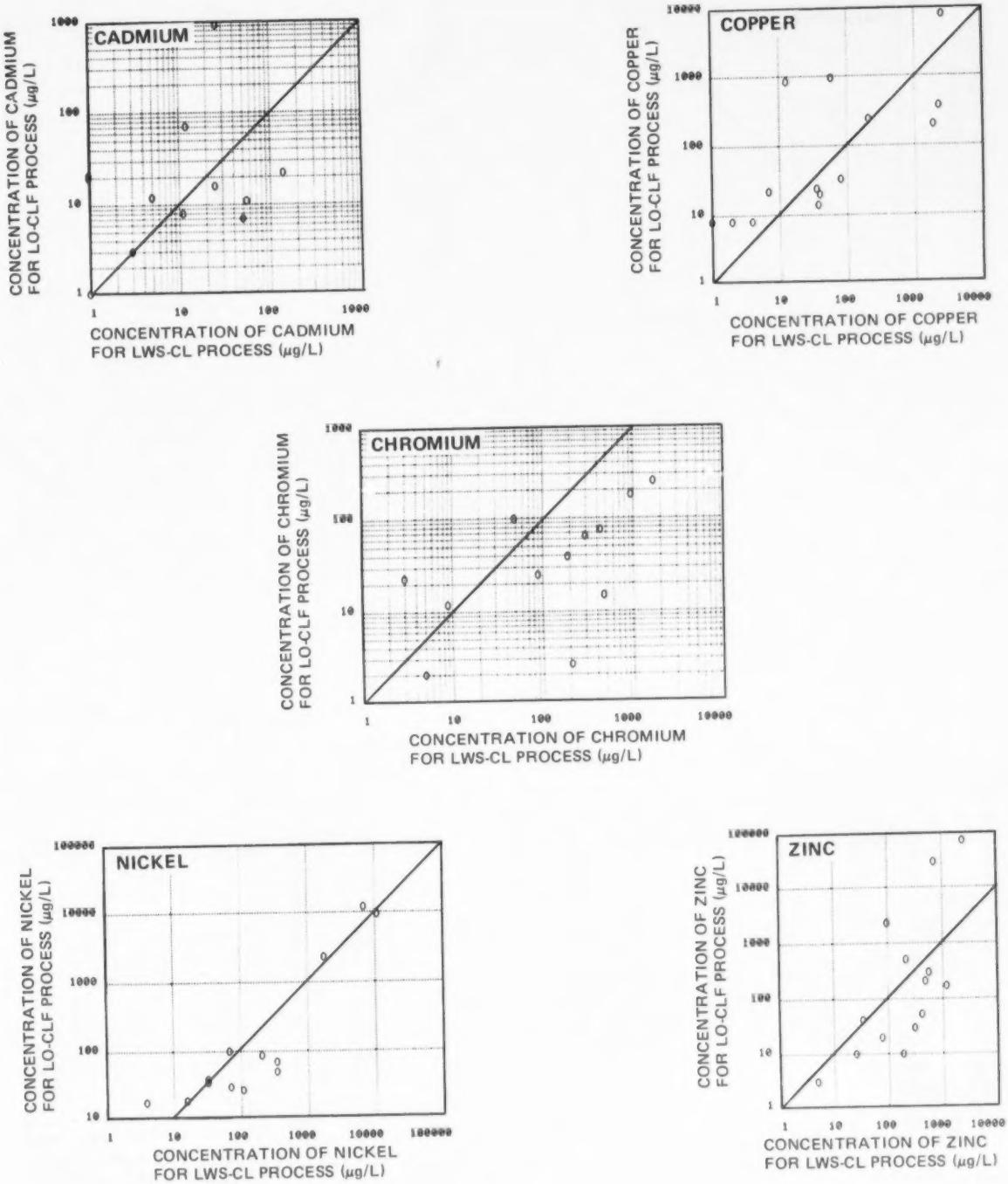

CADMIUM
CONCENTRATION OF CADMIUM FOR LO-CLF PROCESS (µg/L)
CONCENTRATION OF CADMIUM FOR LWS-CL PROCESS (µg/L)
COPPER
CONCENTRATION OF COPPER FOR LO-CLF PROCESS (µg/L)
CONCENTRATION OF COPPER FOR LWS-CL PROCESS (µg/L)
CHROMIUM
CONCENTRATION OF CHROMIUM FOR LO-CLF PROCESS (µg/L)
CONCENTRATION OF CHROMIUM FOR LWS-CL PROCESS (µg/L)
NICKEL
CONCENTRATION OF NICKEL FOR LO-CLF PROCESS (µg/L)
CONCENTRATION OF NICKEL FOR LWS-CL PROCESS (µg/L)
ZINC
CONCENTRATION OF ZINC FOR LO-CLF PROCESS (µg/L)
CONCENTRATION OF ZINC FOR LWS-CL PROCESS (µg/L)

Figure C-4. Comparison of LWS-CL process and LO-CLF process using Cd, Cu, Cr, Ni, and Zn effluent metal concentrations for all wastewater samples.

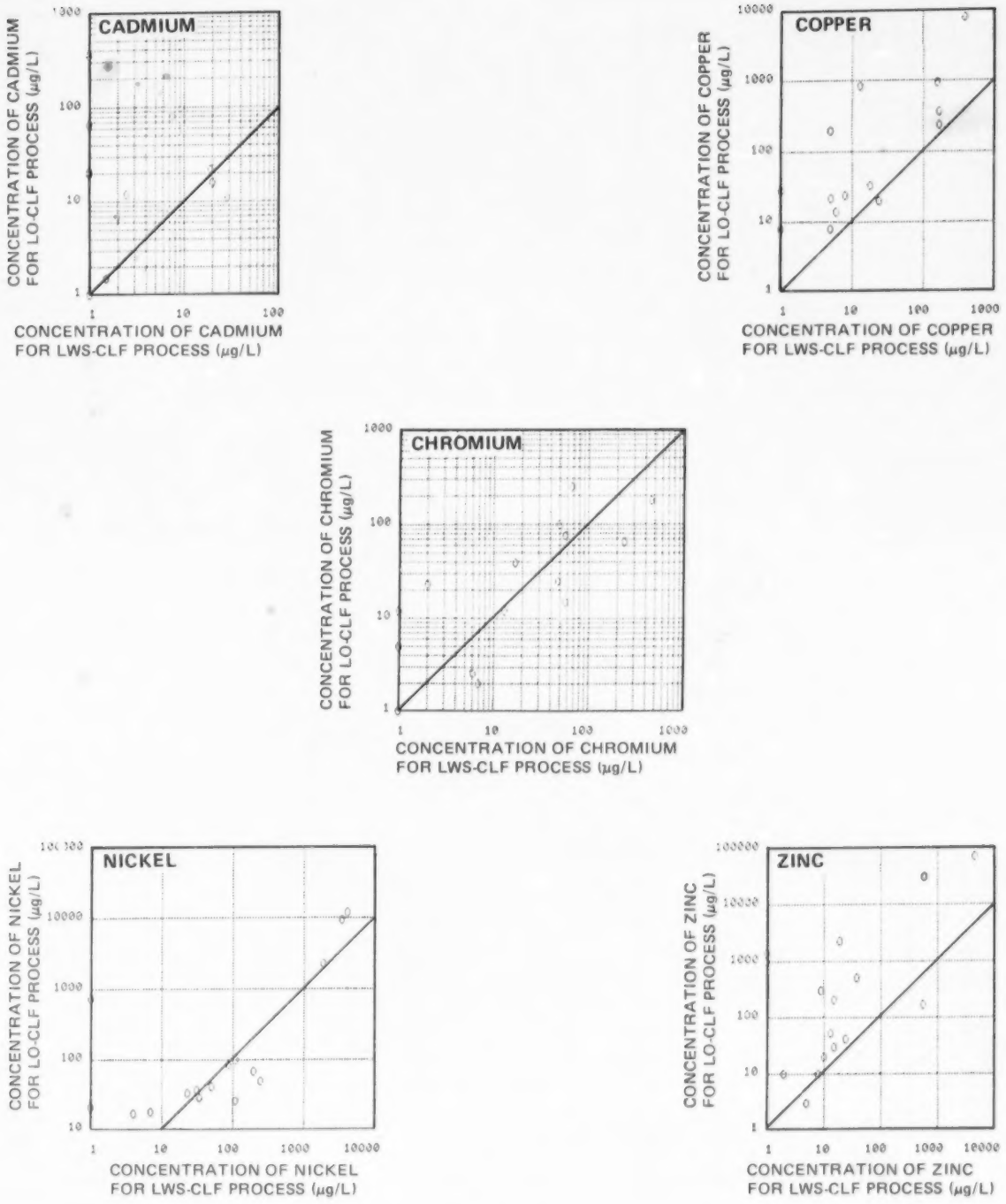

CADMIUM
CONCENTRATION OF CADMIUM FOR LO-CLF PROCESS (µg/L)
CONCENTRATION OF CADMIUM FOR LWS-CLF PROCESS (µg/L)
COPPER
CONCENTRATION OF COPPER FOR LO-CLF PROCESS (µg/L)
CONCENTRATION OF COPPER FOR LWS-CLF PROCESS (µg/L)
CHROMIUM
CONCENTRATION OF CHROMIUM FOR LO-CLF PROCESS (µg/L)
CONCENTRATION OF CHROMIUM FOR LWS-CLF PROCESS (µg/L)
NICKEL
CONCENTRATION OF NICKEL FOR LO-CLF PROCESS (µg/L)
CONCENTRATION OF NICKEL FOR LWS-CLF PROCESS (µg/L)
ZINC
CONCENTRATION OF ZINC FOR LO-CLF PROCESS (µg/L)
CONCENTRATION OF ZINC FOR LWS-CLF PROCESS (µg/L)

Figure C-5. Comparison of LO-CLF process and LWS-CLF process using Cd, Cu, Cr, Ni, and Zn effluent metal concentrations for all wastewater samples.

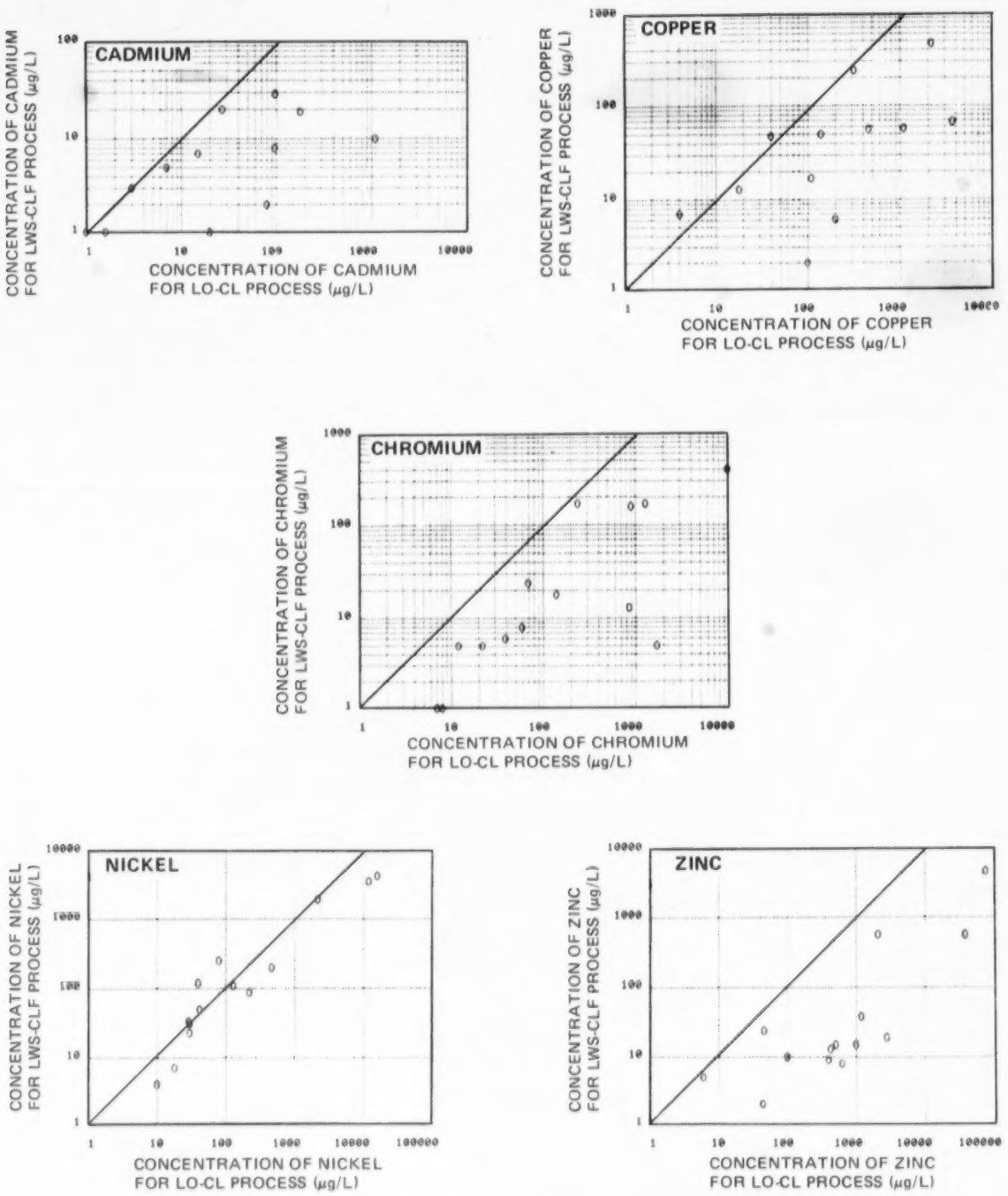

CADMIUM
CONCENTRATION OF CADMIUM FOR LWS-CLF PROCESS (µg/L)
CONCENTRATION OF CADMIUM FOR LO-CL PROCESS (µg/L)
COPPER
CONCENTRATION OF COPPER FOR LWS-CLF PROCESS (µg/L)
CONCENTRATION OF COPPER FOR LO-CL PROCESS (µg/L)
CHROMIUM
CONCENTRATION OF CHROMIUM FOR LWS-CLF PROCESS (µg/L)
CONCENTRATION OF CHROMIUM FOR LO-CL PROCESS (µg/L)
NICKEL
CONCENTRATION OF NICKEL FOR LWS-CLF PROCESS (µg/L)
CONCENTRATION OF NICKEL FOR LO-CL PROCESS (µg/L)
ZINC
CONCENTRATION OF ZINC FOR LWS-CLF PROCESS (µg/L)
CONCENTRATION OF ZINC FOR LO-CL PROCESS (µg/L)

Figure C-6. Comparison of LO-CL process and LWS-CLF process using Cd, Cu, Cr, Ni, and Zn effluent metal concentrations for all wastewater samples.

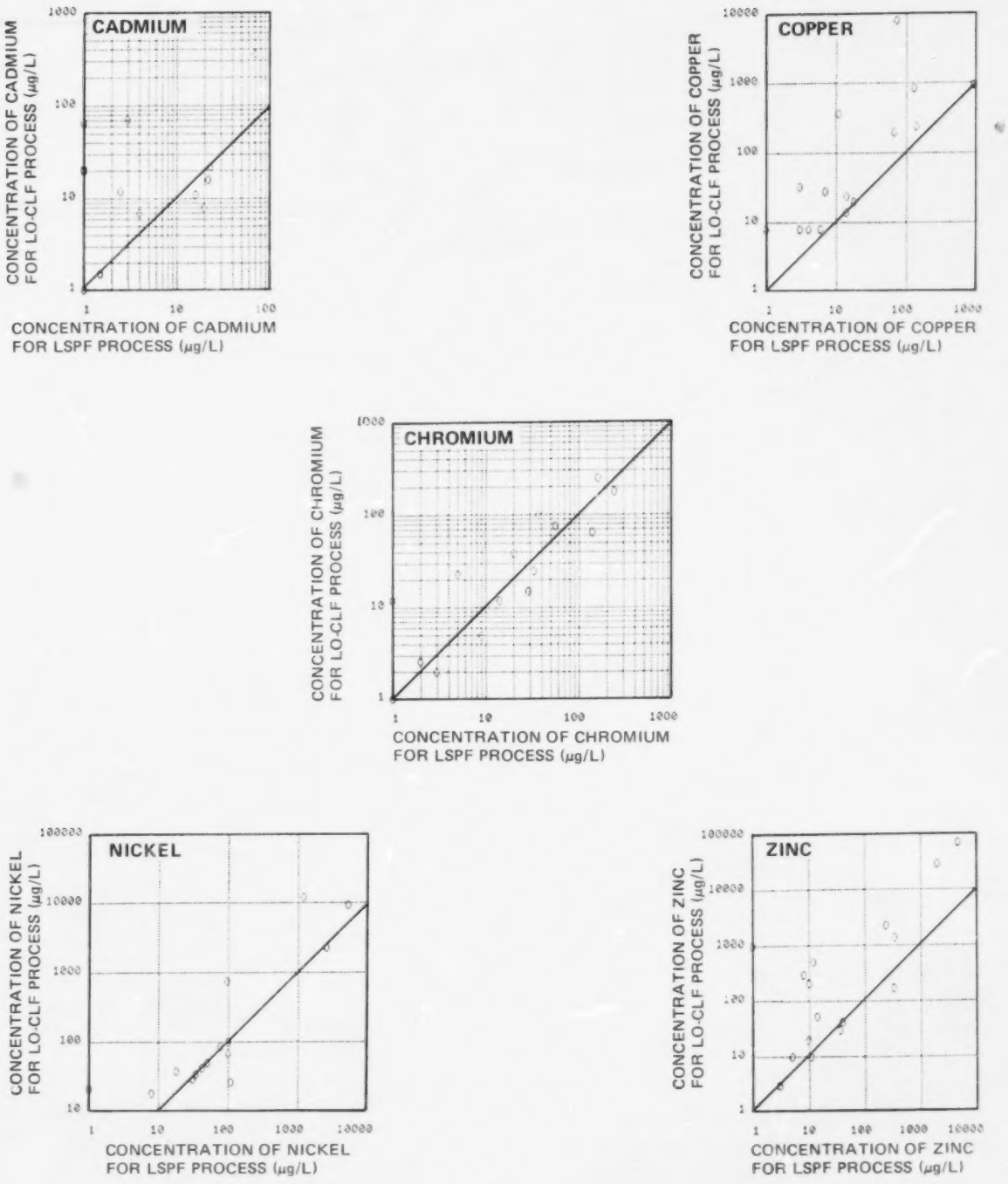

CADMIUM
CONCENTRATION OF CADMIUM FOR LO-CLF PROCESS (µg/L)
CONCENTRATION OF CADMIUM FOR LSPF PROCESS (µg/L)
COPPER
CONCENTRATION OF COPPER FOR LO-CLF PROCESS (µg/L)
CONCENTRATION OF COPPER FOR LSPF PROCESS (µg/L)
CHROMIUM
CONCENTRATION OF CHROMIUM FOR LO-CLF PROCESS (µg/L)
CONCENTRATION OF CHROMIUM FOR LSPF PROCESS (µg/L)
NICKEL
CONCENTRATION OF NICKEL FOR LO-CLF PROCESS (µg/L)
CONCENTRATION OF NICKEL FOR LSPF PROCESS (µg/L)
ZINC
CONCENTRATION OF ZINC FOR LO-CLF PROCESS (µg/L)
CONCENTRATION OF ZINC FOR LSPF PROCESS (µg/L)

Figure C-7. Comparison of LSPF process and LO-CLF process using Cd, Cu, Cr, Ni, and Zn effluent metal concentrations for all wastewater samples.

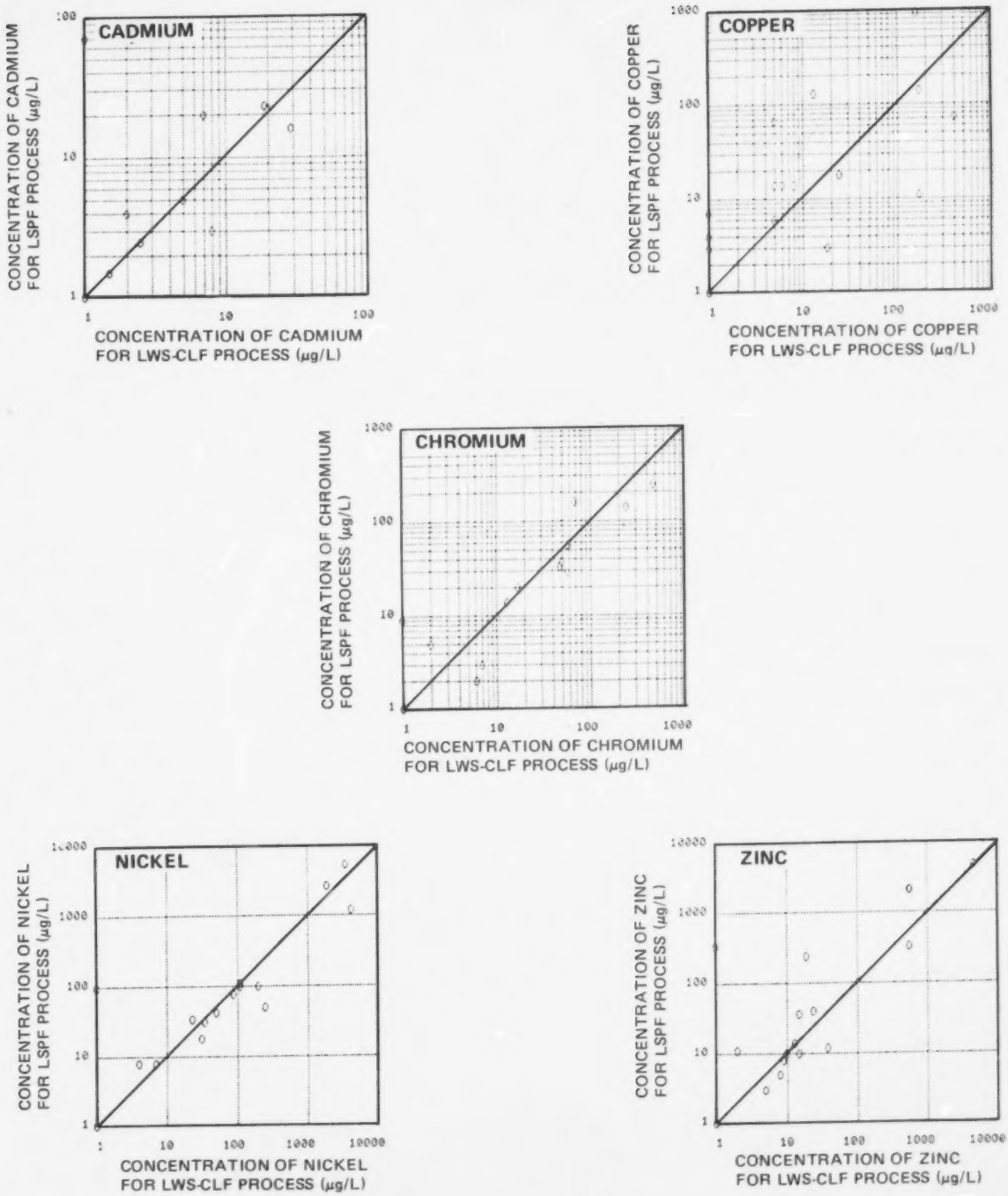

CADMIUM
CONCENTRATION OF CADMIUM FOR LSPF PROCESS (µg/L)
CONCENTRATION OF CADMIUM FOR LWS-CLF PROCESS (µg/L)
COPPER
CONCENTRATION OF COPPER FOR LSPF PROCESS (µg/L)
CONCENTRATION OF COPPER FOR LWS-CLF PROCESS (µg/L)
CHROMIUM
CONCENTRATION OF CHROMIUM FOR LSPF PROCESS (µg/L)
CONCENTRATION OF CHROMIUM FOR LWS-CLF PROCESS (µg/L)
NICKEL
CONCENTRATION OF NICKEL FOR LSPF PROCESS (µg/L)
CONCENTRATION OF NICKEL FOR LWS-CLF PROCESS (µg/L)
ZINC
CONCENTRATION OF ZINC FOR LSPF PROCESS (µg/L)
CONCENTRATION OF ZINC FOR LWS-CLF PROCESS (µg/L)

Figure C-8. Comparison of LWS-CLF process and LSPF process using Cd, Cu, Cr, Ni, and Zn effluent metal concentrations for all wastewater samples.

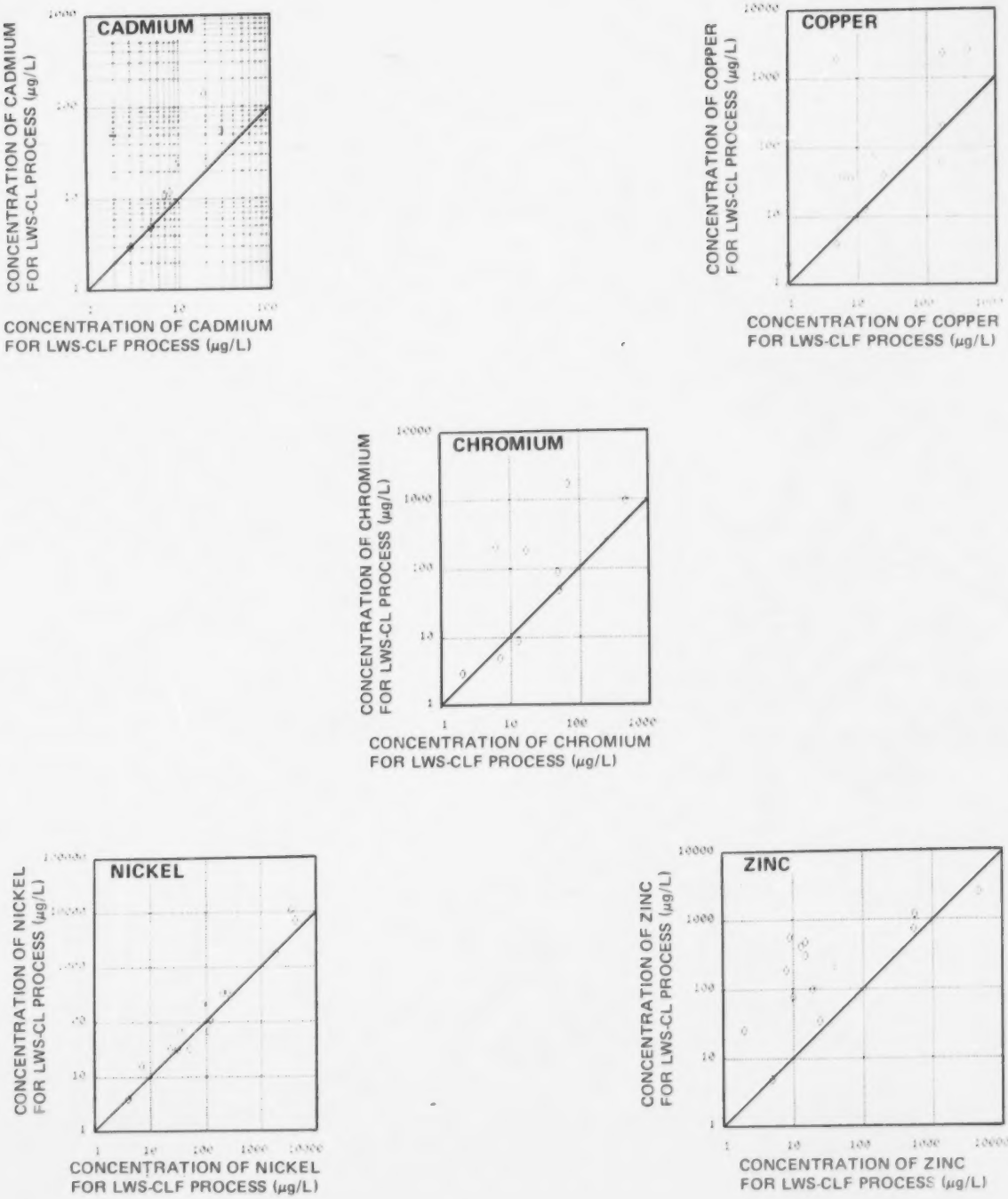

CADMIUM
CONCENTRATION OF CADMIUM FOR LWS-CL PROCESS (µg/L)
CONCENTRATION OF CADMIUM FOR LWS-CLF PROCESS (µg/L)
COPPER
CONCENTRATION OF COPPER FOR LWS-CL PROCESS (µg/L)
CONCENTRATION OF COPPER FOR LWS-CLF PROCESS (µg/L)
CHROMIUM
CONCENTRATION OF CHROMIUM FOR LWS-CL PROCESS (µg/L)
CONCENTRATION OF CHROMIUM FOR LWS-CLF PROCESS (µg/L)
NICKEL
CONCENTRATION OF NICKEL FOR LWS-CL PROCESS (µg/L)
CONCENTRATION OF NICKEL FOR LWS-CLF PROCESS (µg/L)
ZINC
CONCENTRATION OF ZINC FOR LWS-CL PROCESS (µg/L)
CONCENTRATION OF ZINC FOR LWS-CLF PROCESS (µg/L)

Figure C-9. Comparison of LWS-CLF process and LWS-CL process using Cd, Cu, Cr, Ni, and Zn effluent metal concentrations for all wastewater samples.

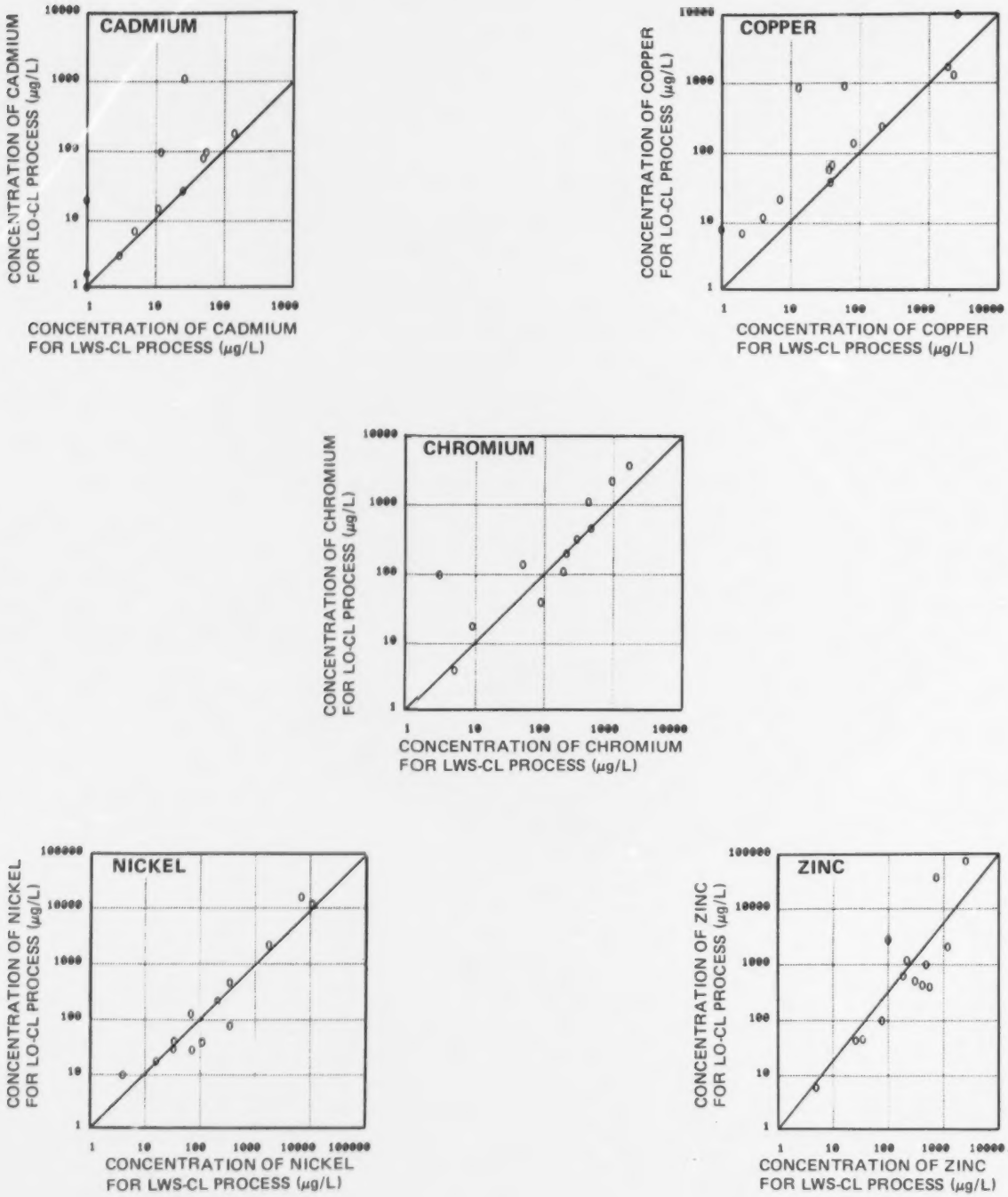

CADMIUM
CONCENTRATION OF CADMIUM FOR LO-CL PROCESS (µg/L)
CONCENTRATION OF CADMIUM FOR LWS-CL PROCESS (µg/L)
COPPER
CONCENTRATION OF COPPER FOR LO-CL PROCESS (µg/L)
CONCENTRATION OF COPPER FOR LWS-CL PROCESS (µg/L)
CHROMIUM
CONCENTRATION OF CHROMIUM FOR LO-CL PROCESS (µg/L)
CONCENTRATION OF CHROMIUM FOR LWS-CL PROCESS (µg/L)
NICKEL
CONCENTRATION OF NICKEL FOR LO-CL PROCESS (µg/L)
CONCENTRATION OF NICKEL FOR LWS-CL PROCESS (µg/L)
ZINC
CONCENTRATION OF ZINC FOR LO-CL PROCESS (µg/L)
CONCENTRATION OF ZINC FOR LWS-CL PROCESS (µg/L)

Figure C-10. Comparison of LWS-CL process and LO-CL process using Cd, Cu, Cr, Ni, and Zn effluent metal concentrations for all wastewater samples.

APPENDIX D

SIGN TEST STATISTICAL ANALYSIS

Sign test statistical analyses were performed to establish a hierarchy (charted in Figure D-1) to rank the five wastewater treatment processes. The hierarchy was based on cadmium, copper, chromium, nickel, and zinc effluent concentration data from the 16 test runs.

The hierarchy was established by successively selecting and comparing two processes to determine if the pair gave significantly different results and then ranking the processes accordingly. For example, the LSPF process was compared to the LWS-CL process. For each of the 16 test runs, a set of five matched pairs was established by pairing the Cd effluent concentration of the LSPF process with the Cd effluent concentration of the LWS-CL process; the Cu effluent concentration of the LSPF process with the Cu effluent concentration of the LWS-CL process; and similarly, for Cr, Ni, and Zn. Thus, a set of about 80 matched pairs was established for the sign test. They were used to determine which two processes produce significantly different effluent concentration levels. Successive pairs of processes were compared until the hierarchy chart (Figure D-1) was completely established.

The results of the sign test analyses on sets of matched pairs are shown in Figures D-2 through D-11.

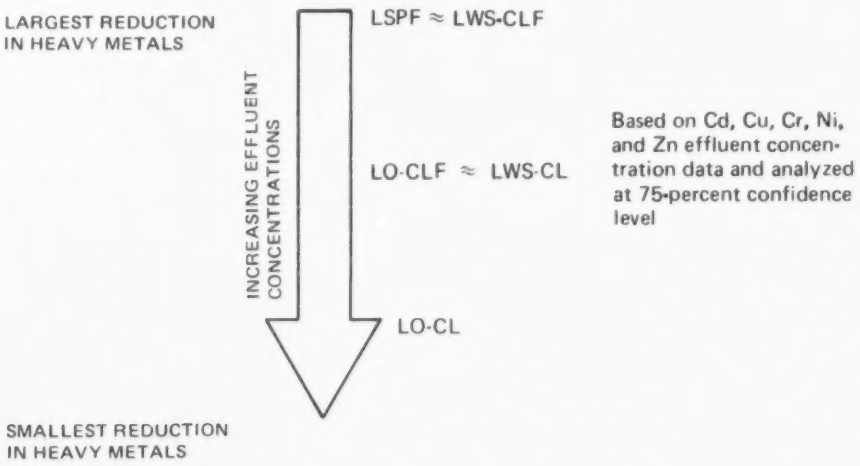
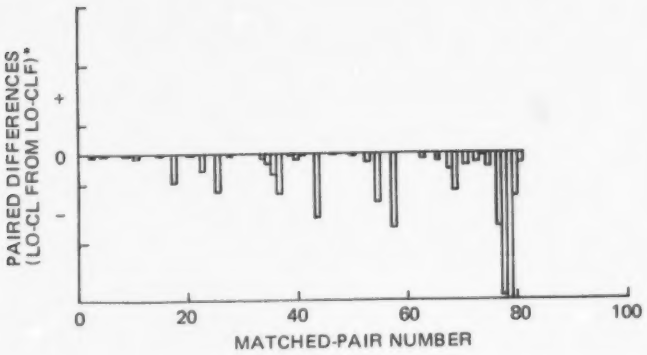
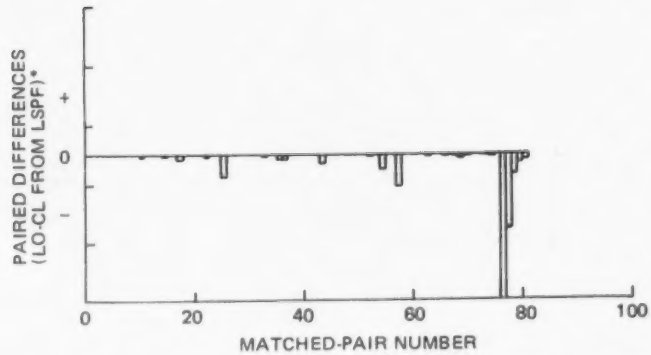

LARGEST REDUCTION IN HEAVY METALS
LSPF ≈ LWS-CLF
INCREASING EFFLUENT CONCENTRATIONS
LO-CLF ≈ LWS-CL
Based on Cd, Cu, Cr, Ni, and Zn effluent concentration data and analyzed at 75-percent confidence level
LO-CL
SMALLEST REDUCTION IN HEAVY METALS

Figure D-1. Hierarchy of wastewater treatment processes established from sign test statistical analysis.



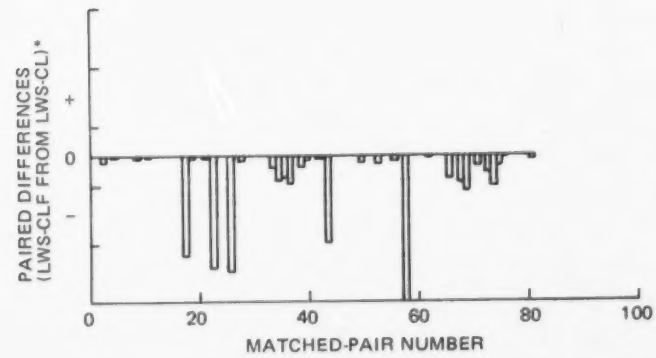
- Number of positive differences: 7
- Number of negative differences: 59
- Computed Z-statistic: 6.278
- Tabled Z-value: 1.150

Figure D-2. Agreement between LO-CLF and LO-CL not significant at 75-percent confidence level.



- Number of positive differences: 6
- Number of negative differences: 63
- Computed Z-statistic: 6.742
- Tabled Z-value: 1.150

Figure D-3. Agreement between LSPF and LO-CL not significant at 75-percent confidence level.



- Number of positive differences: 10
- Number of negative differences: 47
- Computed Z-statistic: 4.768
- Tabled Z-value: 1.150

Figure D-4. Agreement between LWS-CL and LWS-CLF not significant at 75-percent confidence level.

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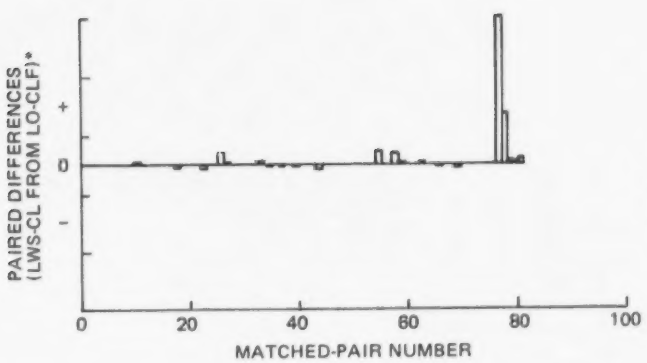
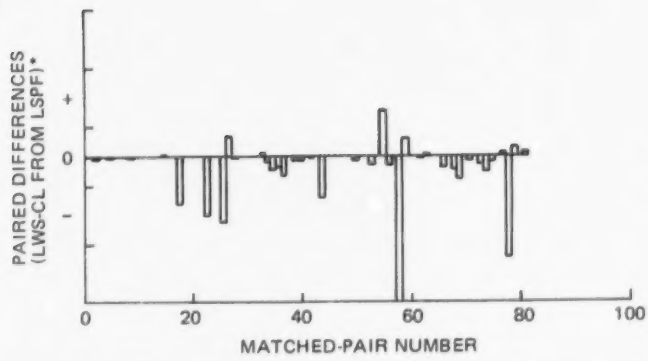
* Differences between effluent concentrations (Cd, Cu, Cr, Ni, and Zn) of paired processes



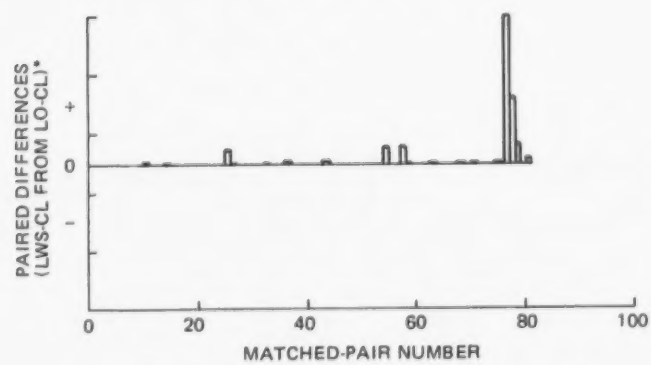
- Number of positive differences: 29
- Number of negative differences: 35
- Computed Z-statistic: 0.625
- Tabled Z-value: 1.150

Figure D-5. Agreement between LO-CLF and LWS-CL significant at 75-percent confidence level.



- Number of positive differences: 19
- Number of negative differences: 42
- Computed Z-statistic: 2.817
- Tabled Z-value: 1.150

Figure D-6. Agreement between LSPF and LWS-CL not significant at 75-percent confidence level.

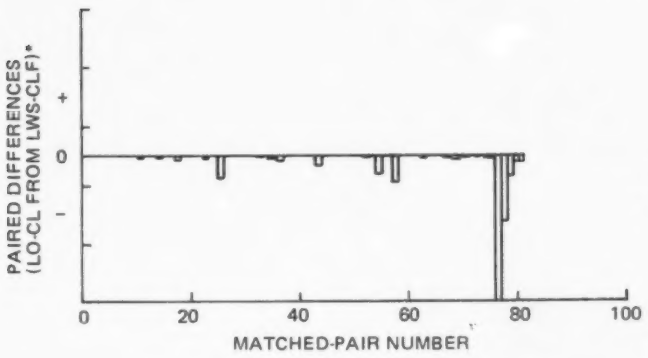


- Number of positive differences: 52
- Number of negative differences: 13
- Computed Z-statistic: 4.713
- Tabled Z-value: 1.150

Figure D-7. Agreement between LO-CL and LWS-CL not significant at 75-percent confidence level.

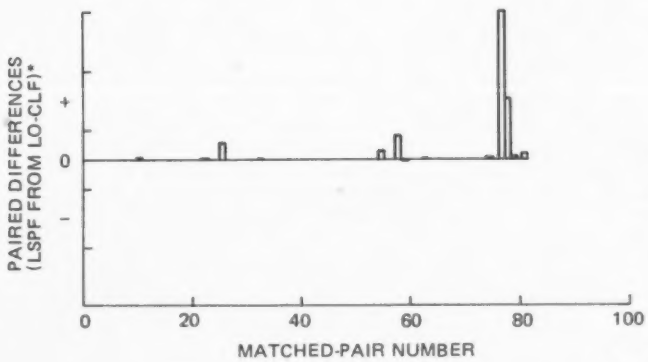
---

* Differences between effluent concentrations (Cd, Cu, Cr, Ni, and Zn) of paired processes



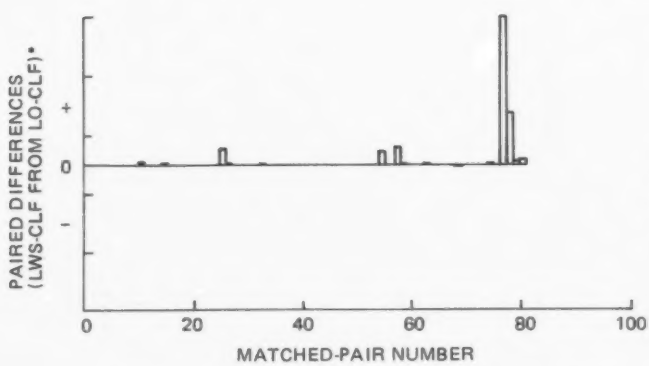
- Number of positive differences: 7
- Number of negative differences: 58
- Computed Z-statistic: 6.202
- Tabled Z-value: 1.150

Figure D-8. Agreement between LWS-CLF and LO-CL not significant at 75-percent confidence level.



- Number of positive differences: 45
- Number of negative differences: 18
- Computed Z-statistic: 3.276
- Tabled Z-value: 1.150

Figure D-9. Agreement between LO-CLF and LSPF not significant at 75-percent confidence level.



- Number of positive differences: 45
- Number of negative differences: 19
- Computed Z-statistic: 3.125
- Tabled Z-value: 1.150

Figure D-10. Agreement between LO-CLF and LWS-CLF not significant at 75-percent confidence level.

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* Differences between effluent concentrations (Cd, Cu, Cr, Ni, and Zn) of paired processes

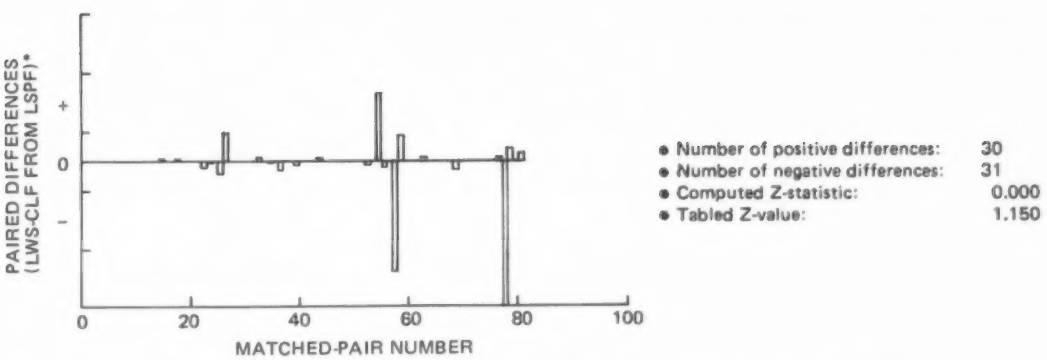


Figure D-11. Agreement between LSPF and LWS-CLF significant at 75-percent confidence level.

* Differences between effluent concentrations (Cd, Cu, Cr, Ni, and Zn) of paired processes

APPENDIX E

WILCOXON MATCHED-PAIR, SIGNED-RANK STATISTICAL ANALYSIS

The Wilcoxon matched-pair, signed-rank statistical method (13) was used to establish the hierarchy chart (Figure E-1) to rank the five wastewater treatment processes. The hierarchy was based on cadmium, copper, chromium, nickel, and zinc effluent concentration data from the 16 test runs.

The hierarchy was established by determining if a pair of processes gave significantly different results. The processes were ranked accordingly. For example, the LSPF process was compared to the LWS-CL process. For each of the 16 test runs, a set of five matched pairs was established by pairing the Cd effluent concentration of the LSPF process with the Cd effluent concentration of the LWS-CL process; the Cu effluent concentration of the LSPF process with the Cu effluent concentration of the LWS-CL process; and similarly, for Cr, Ni, and Zn. Thus, a set of about 80 matched pairs was established for the Wilcoxon method. They were used to determine which two processes produced significantly different effluent concentration levels, based on the T-value reported in Table E-1.

The signed ranks indicated that the LSPF process produced lower effluent concentration levels than those of the LWS-CL process. Thus, the LSPF process was ranked above the LWS-CL process on the hierarchy chart. If the two processes did not produce significantly different results, the processes would have had the same rank on the hierarchy chart, as in the comparison of the LSPF process to the LWS-CLF process. Successive pairs of processes were compared until the hierarchy chart (Figure E-1) was completely established.

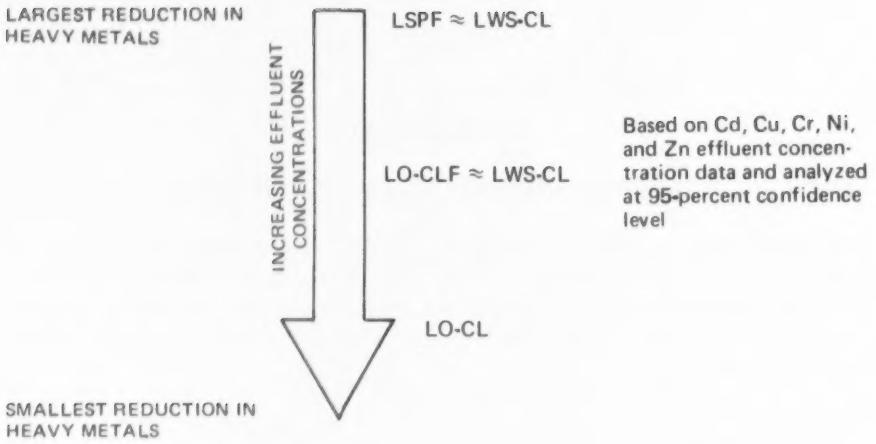

LARGEST REDUCTION IN HEAVY METALS
INCREASING EFFLUENT CONCENTRATIONS
LSPF ≈ LWS-CL
LO-CLF ≈ LWS-CL
LO-CL
Based on Cd, Cu, Cr, Ni, and Zn effluent concentration data and analyzed at 95-percent confidence level
SMALLEST REDUCTION IN HEAVY METALS

Figure E-1. Hierarchy of wastewater treatment processes established from Wilcoxon matched-pair, signed-rank statistical analysis (ref. 13).

TABLE E-1. T-VALUES OF WILCOXON MATCHED-PAIR, SIGNED-RANK STATISTICAL ANALYSIS

Comparison pair	T-value calculated from experimental data (smaller sum of like-signed ranks) *	$T_{0.5}$-value required for a significant difference at 95% confidence level †	Significant difference at 95% confidence level
LO-CL and LO-CLF	108	848	Yes
LSPF and LWS-CL	411	717	Yes
LO-CL and LWS-CL	401	821	Yes
LSPF and LWS-CLF	868	717	No
LWS-CL and LWS-CLF	195	620	Yes
LO-CLF and LSPF	385	643	Yes
LO-CLF and LWS-CL	848	794	No
LO-CLF and LWS-CLF	495	794	Yes

* Includes data for only cadmium, copper, chromium, nickel, and zinc heavy metals.

† When the T-value calculated from the experimental data exceeds the $T_{0.5}$-value, the two processes are not significantly different at the 95% confidence level.

APPENDIX F

CAPITAL COST OF FULL-SCALE PLANTS

The full-scale plants outlined in this appendix were used to provide the basis for capital equipment cost comparisons. The plants do not include cyanide destruction systems or hexavalent chromium reduction systems; such processes would be a cost burden on all five processes. This appendix includes plant schematics, layout drawings, and construction details.

LIST OF FIGURES

F-1 Small LO-CL and LO-CLF plant schematic
F-2 Small LSPF, LWS-CL, and LWS-CLF plant schematic
F-3 Medium-sized LO-CL and LO-CLF plant schematic
F-4 Medium-sized LSPF plant schematic
F-5 Medium-sized LWS-CL and LWS-CLF plant schematic
F-6 Large LO-CL and LO-CLF plant schematic
F-7 Large LSPF plant schematic
F-8 Large LWS-CL and LWS-CLF plant schematic
F-9 Small plant layout—all processes (LO-CL, LO-CLF, LSPF, LWS-CL, and LWS-CLF)
F-10 Medium-sized LO-CL and LO-CLF plant layout
F-11 Medium-sized LSPF plant layout
F-12 Medium-sized LWS-CL and LWS-CLF plant layout
F-13 Large LO-CL and LO-CLF plant layout
F-14 Large LSPF plant layout
F-15 Large LWS-CL and LWS-CLF plant layout
F-16 Cross section of medium-sized and large plants—all processes (LO-CL, LO-CLF, LSPF, LWS-CL, and LWS-CLF)

ENGINEERING SPECIFICATIONS FOR SMALL PLANTS
(Figures F-1, F-2, and F-9)

A. The leveling storage tank will hold a minimum of one day's effluent and will be acid-resistant. This provides for batch processing, which is the most economical method for this flow rate.

B. The mixer-clarifier tank will hold the same amount of effluent as tank A. Tank B is to be acid-resistant lined and will also contain an acid-resistant coated mixer. For convenient sludge removal, this tank must have a tapered bottom with a view-port for observation of the sludge bed level. Manually controlled pH levels are tested in the lab. Sulfide and H_2S levels are controlled manually as determined by an automatic H_2S gas detector. Upon completion of sludge removal to the filter press, item C, the effluent is discharged in the following manner: to the sewer (LO-CL

process); to the filter (LO-CLF process); to the aerator (LWS-CL process); and to the filter and aerator (LSPF and LWS-CLF processes).

C. The filter press dewaters the sludge to 60-percent moisture content. Means for sludge removal are to be provided.

D. The aerator is used to oxygenate the effluent before discharge; the rate depends upon system size.

E. The filter is a manifold type for small particulate removal.

F. An automatic audible alarm must be installed in the process area to signal when tank levels are too high and to detect H_2S gas.

G. Flow control should be kept to specifications for efficient operation.

H. An instrument control panel must be easily accessible to the operator and centrally located to the treatment area. Instruments installed on the panel must include the following:
   H.1. On-off control of all pumps.
   H.2. Indicators of water levels in each tank, including a yellow light for above-normal levels and a red emergency light for critical water levels.
   H.3. A flow diagram of the treatment plant process with lights that indicate equipment operation status: green for equipment operating and valves in normal position, red for equipment "off" and valves redirecting flow, plus flashing red for automatic pump switchover.

I. For the lab, sufficient equipment must be provided to perform pH titrations and sulfide and H_2S detection.

J. Adequate storage space (to be as safe as reasonable) must be provided for all needed process chemicals.

K. For emergency and safety provisions, a sump should be provided, with the tank farm curbed off in case of accident. Emergency lights must be provided for the control panel and for the process area.

L. Automatic switchover must be provided for all pumps in case of failure. The pump between tanks A and B should be acid-resistant.

M. All valves are manual, with one acid-resistant valve before tank A.

N. Acid-resistant pipe is to be provided wherever it may contact untreated wastewater.

Flow rate is assumed to be as indicated in system specifications. An allowance for equipment for double-pump automatic switchover was not taken into account. All pumps have been located in the storage area to avoid exposure to weather, thus contributing to ease of maintenance and increased reliability. Because of the low flow rate, this is a batch process. Tne lab is to be used to determine the pH level and the amount of sulfide needed. The amount of polymer needed can also be determined; for this, proper equipment should be provided.

ENGINEERING SPECIFICATIONS FOR MEDIUM-SIZED AND LARGE PLANTS

(Figures F-3 through F-8 and F-10 through F-16)

A. The lagoon is based on a 2.13m (7-ft) depth because of elevation and tidal conditions at a proposed site. An acid-resistant coating is to be installed to protect the lagoon in case of treatment plant breakdown. The use of support pilings around and within the lagoon is suggested. This provides for the construction of a deck covering the lagoon, except for a grate that surrounds the treatment plant proper.

B. The deck should be constructed to support the weight of the treatment plant. The area directly under the plant should be constructed to withstand at least 4,880 kg/m² (1,000 lb/ft²), and the remaining area, at least 488 kg/m² (100 lb/ft²).

C. The treatment plant includes the following:

C.1 The leveling tank is to be lined with an acid-resistant coating. This is the first stop for the plant wastewater, unless the wastewater is directed to the lagoon.

C.2 The flash mixer is to be lined with an acid-resistant coating; the mixing blade is to be coated also. A roof, having H_2S detectors, should be provided for the flash mixer.

C.3 The lime store area is an elevated tank for unslaked lime; the raised position provides for easy transport to the C-2 area. The tank is to be attached to the control room building for added support.

C.3.1 The lime slaker mixes fresh, slaked lime and water and passes this lime slurry to a slurry tank. (The manufacturer-supplied system includes pumps, pipes, and slaker.)

C.3.2 The lime slurry tank is used for continuous flow to either tank B or recycle. (The manufacturer-supplied system includes pumps, tank, and piping up to, and including, the valve.) The valve must be electrically operated for control by the pH system.

C.3.3 The pH control area is to contain the pH control machinery (automatic and manual). This includes pH level monitors, controllers, and recorders. The pH sensors are to be located on the pipe leading to tank B from tank A and on the line leaving tank B.

C.4 The polymer feed area includes the mixer, tank, and pipes up to and including the pumps; this is a continuous process at a designated flow.

C.5 The flocculating tank receives flow from tank B and the polymer feed system. The tank located on top of the clarifier, is arranged so that overflow will cascade into the clarifier.

C.6 The clarifier is furnished by the manufacturer and receives flow from the flocculator and the filter press. The sludge contracted at the clarifier bottom flows to the sludge storage tank (tank H) by a pump. The clarifier overflow drains into the sewer.

C.6.1 Clarifier overflow goes to the aerator, tank K, by gravity feed (for sulfide treatment system only).

C.6.2 Clarifier overflow goes to the aerator, tank J-3, by gravity feed (for sulfide polish system only).

C.7 The sludge storage tank is designed to hold a day-to-day supply of sludge for batch processing by the filter press, according to the recommended procedure.

C.8 The filter press is a manufactured item that can process a 2-day supply of sludge in 12 hr. Means for sludge removal are to be provided. Removed water is recirculated to the clarifier; this flow can also be directed to the lagoon for dilution or complete reprocessing. Sludge is dewatered to 60-percent moisture content.

C.9 The sulfide feed system is supplied by the manufacturer; it includes tank, motors, pumps, and pipe up to and including the valve (to be electrically operated). (The system is for sulfide treatment and sulfide polish systems only.)

C.9.1 The sulfide control area is to contain the sulfide control machinery (automatic and manual); this includes monitors, controllers, and recorders. Free-sulfide and H_2S level sensors should be installed:

C.9.1.a On the pipe between tanks A and B, and between tanks B and C (for sulfide treatment system only);

C.9.1.b On the line between tanks G and J-3, and between tanks J-3 and L (for sulfide polish system only).

C.9.2 The sulfide slurry tank is a mixer and should have H_2S gas detection equipment installed around it. The tank receives flow from the clarifier and sulfide feed tank, which feeds to a filter (manifold type). (The tank is for the sulfide polish system only.)

C.10 The aerator oxygenates the effluent before discharge. The rate depends on system size. (For sulfide treatment and sulfide polish systems only.)

C.11 The filter is a manifold type for small particulate removal to be discharged into the aerator. (For the sulfide polish system only.)

D. An audible alarm and an automatic process water detour are needed. An audible signal must be installed in the process area to sound when the water in the tanks reaches critical levels, when the pH level is too acid for the process, or when H_2S gas is detected. The main valve at the plant process water inlet must automatically detour process water to the lagoon.

E. The flow control should be kept to specifications for efficient operations.

F. An instrument control panel must be easily accessible to the operator and centrally located to the treatment equipment. Instruments installed on the panel must include the following:

F.1 On-off control of all pumps.

F.2 Indicators of water levels in each tank, including a yellow light for above-normal levels and a red emergency light for critical water levels.

F.3 A flow diagram of the treatment plant process with lights that indicate equipment operating status: green for equipment operating and valves in normal position, red for equipment "off" and valves redirecting flow, plus flashing red for automatic pump switchover. Remote indicators must be provided for all pH and sulfide readings and for H_2S gas monitors.

G. Adequate storage space is to be allotted for all chemical storage in safe, controlled areas as near as practical to the location of use.

H. For emergency and safety provisions, the plant must contain the following:
   H.1 Backup dust equipment must be provided, including switching, valves, and controls to operate properly.
   H.2 Emergency lights must be displayed on the control panel and in the manufacturing process area as described under indicators (F.2).

I. For pumps, automatic switchover must be provided in case of failure. Some pumps should be as acid-resistant as possible, depending on their location in the system.

J. All necessary safety valves should be included. The valve on the effluent receiving side of tank A should be electrically operated and as acid-resistant as possible, or coated; the same holds true for the valve on the outlet side of tank A.

K. All pipe that will contact untreated wastewater is to have an acid-resistant liner and, in the case of lagoon pipes, an acid-resistant coating.

Flow rate is assumed to be as indicated in system specifications. Allowance for equipment for double-pump automatic switchover was not taken into account. All pumps have been located in the storage area to avoid exposure to weather, thus contributing to ease of maintenance and increased reliability.

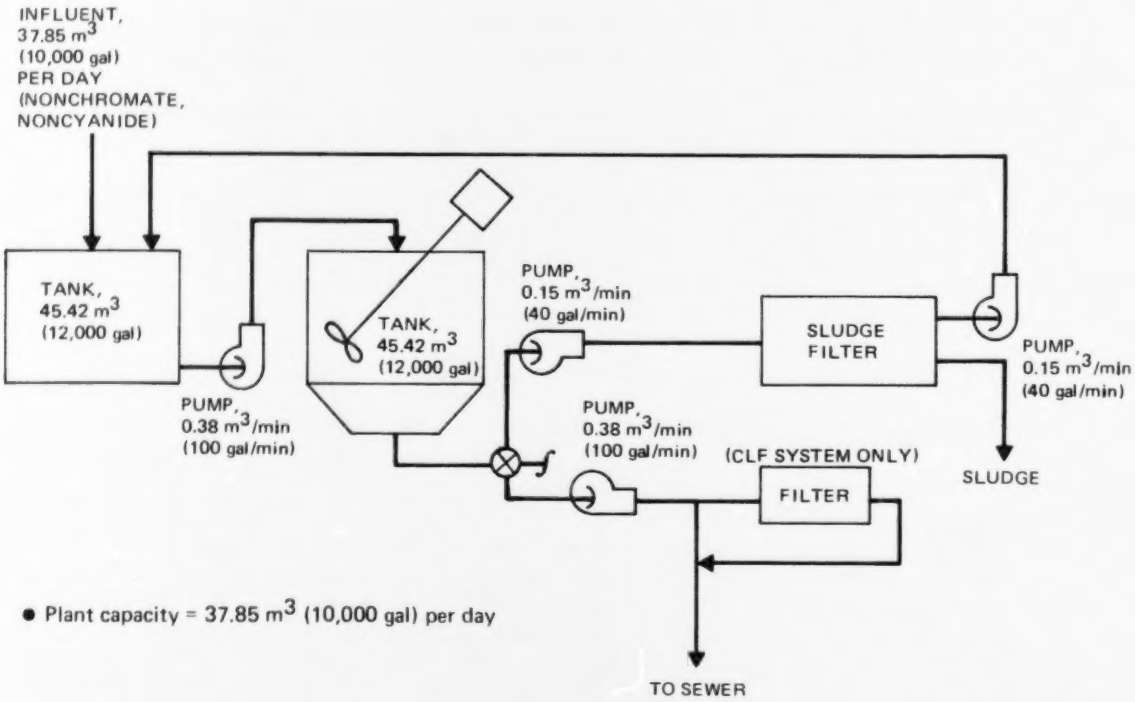

INFLUENT, 37.85 m3 (10,000 gal) PER DAY (NONCHROMATE, NONCYANIDE)
TANK, 45.42 m3 (12,000 gal)
PUMP, 0.38 m3/min (100 gal/min)
TANK, 45.42 m3 (12,000 gal)
PUMP, 0.15 m3/min (40 gal/min)
SLUDGE FILTER
PUMP, 0.15 m3/min (40 gal/min)
SLUDGE
PUMP, 0.38 m3/min (100 gal/min)
(CLF SYSTEM ONLY)
FILTER
• Plant capacity = 37.85 m3 (10,000 gal) per day
TO SEWER

Figure F-1. Small LO-CL and LO-CLF plant schematic.

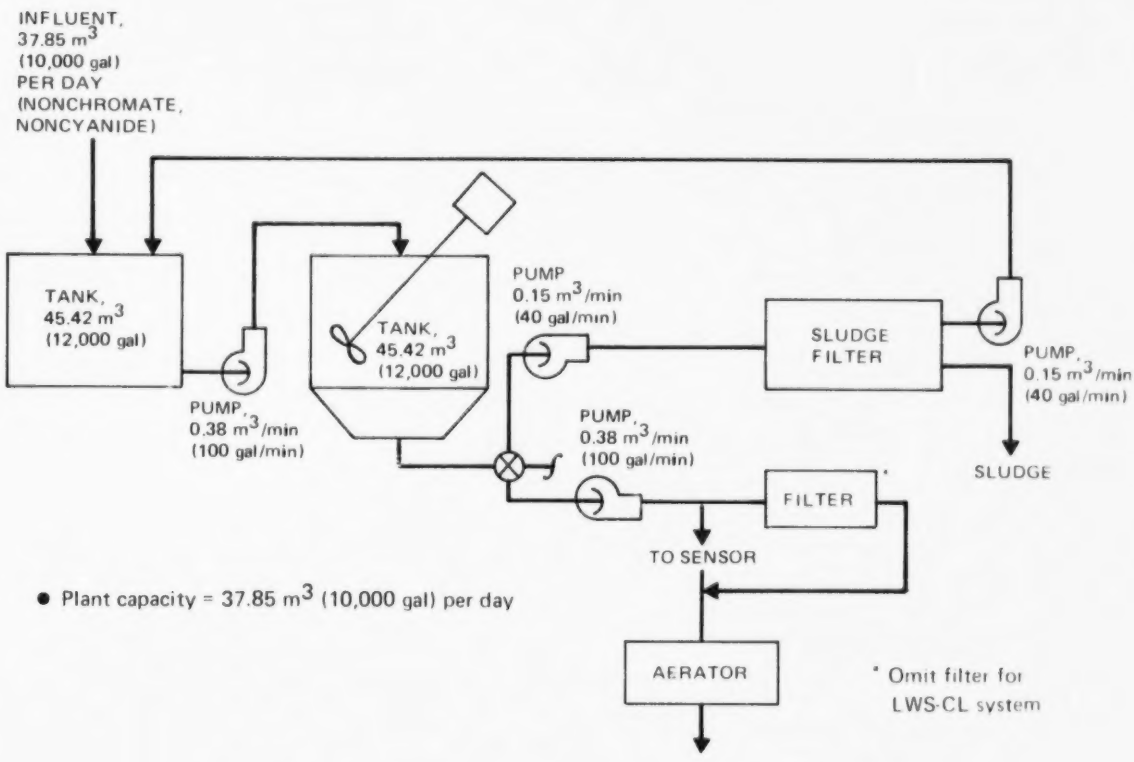


Figure F-2. Small LSPF, LWS-CL, and LWS-CLF plant schematic.

- Plant capacity = 757 m^3 (200,000 gal) per day

- Lagoon – 763 m^3 (201,600 gal)
- Leveling tank – 31.8 m^3 (8,400 gal)
- Lime feed – 0.95 L/min (0.25 gal/min)
- Flash mixer – 5.3 m^3 (1,400 gal)
- Polymer feed – 5.3 L/min (1.4 gal/min)
- Flocculating tank – 2.65 m^3 (700 gal)
- Clarifier – 72.5 m^2 (780 ft^2)
- Sludge filter press – 0.3 m^3 (10.8 ft^3) per day, 60% moisture

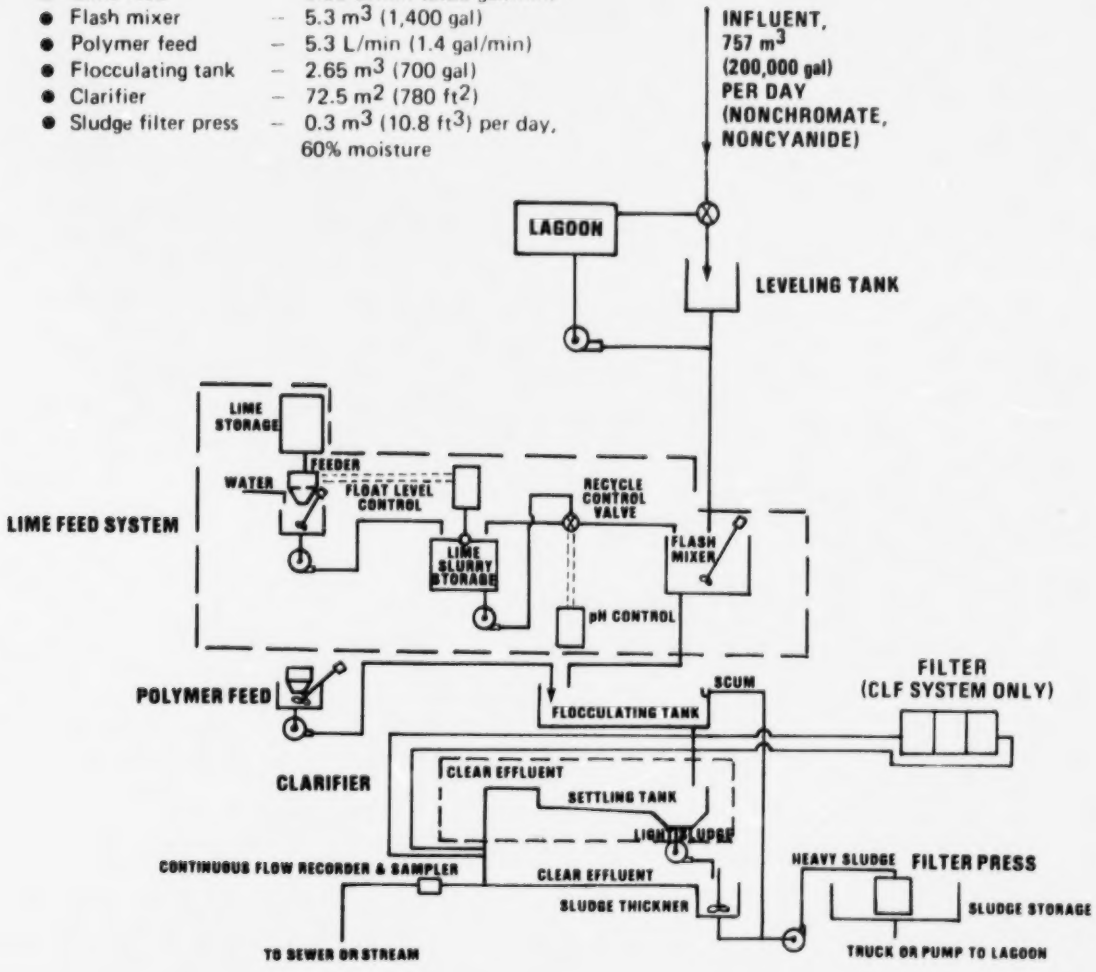


Figure F-3. Medium-sized LO-CL and LO-CLF plant schematic.

- Plant capacity = 757 m^3 (200,000 gal) per day

- Lagoon – 763 m^3 (201,600 gal)
- Leveling tank – 31.8 m^3 (8,400 gal)
- Lime feed – 0.95 L/min (0.25 gal/min)
- Flash mixer – 5.3 m^3 (1,400 gal)
- Polymer feed – 5.3 L/min (1.4 gal/min)
- Flocculating tank – 2.65 m^3 (700 gal)
- Clarifier – 72.5 m^2 (780 ft^2)
- Sludge filter press – 0.3 m^3 (10.8 ft^3) per day, 60% moisture
- Aerator – 0.9g (0.002 lb) per minute of O_2

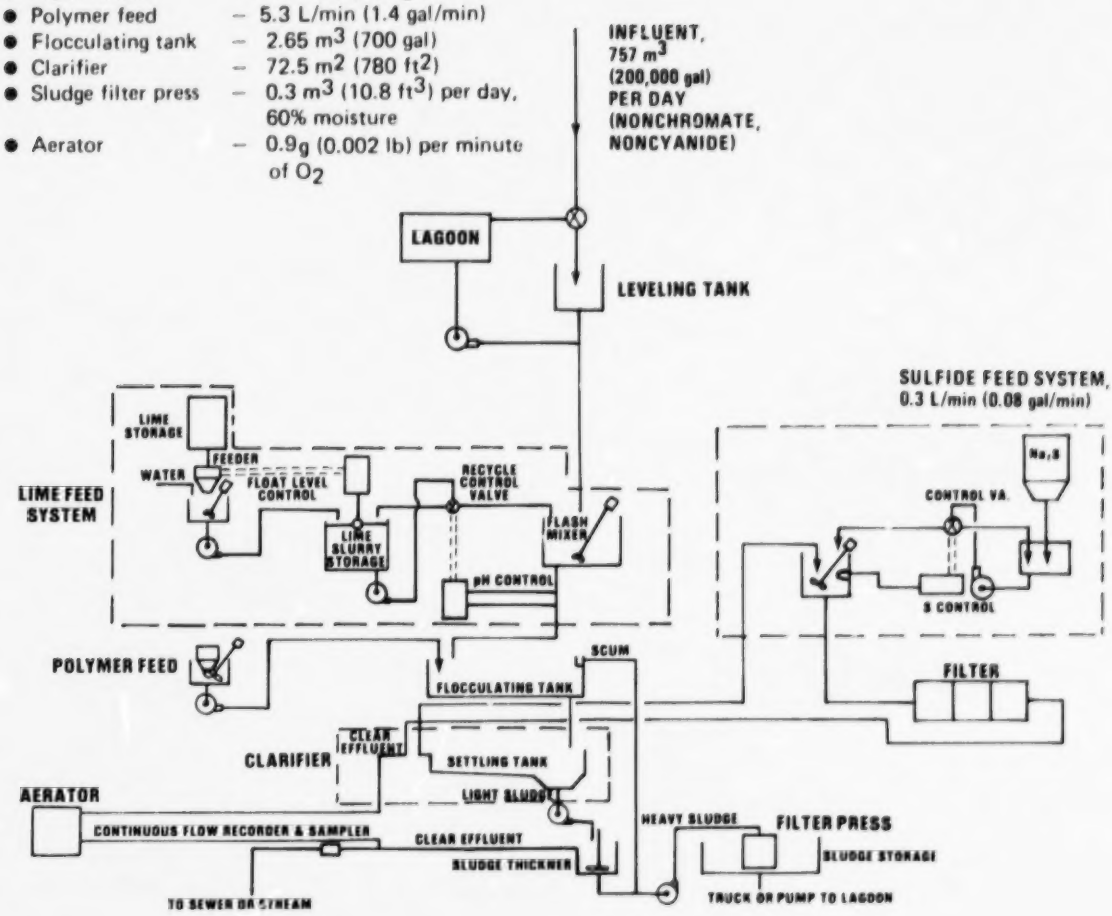


Figure F-4. Medium-sized LSPF plant schematic.

- Plant capacity = 757 m^3 (200,000 gal) per day

- Lagoon – 763 m^3 (201,600 gal)
- Leveling tank – 31.8 m^3 (8,400 gal)
- Lime feed – 0.95 L/min (0.25 gal/min)
- Flash mixer – 5.3 m^3 (1,400 gal)
- Polymer feed – 5.3 L/min (1.4 gal/min)
- Flocculating tank – 2.65 m^3 (700 gal)
- Clarifier – 72.5 m^2 (780 ft^2)
- Sludge filter press – 0.3 m^3 (10.8 ft^3) per day, 60% moisture
- Aerator – 0.9g (0.002 lb) per minute of O_2

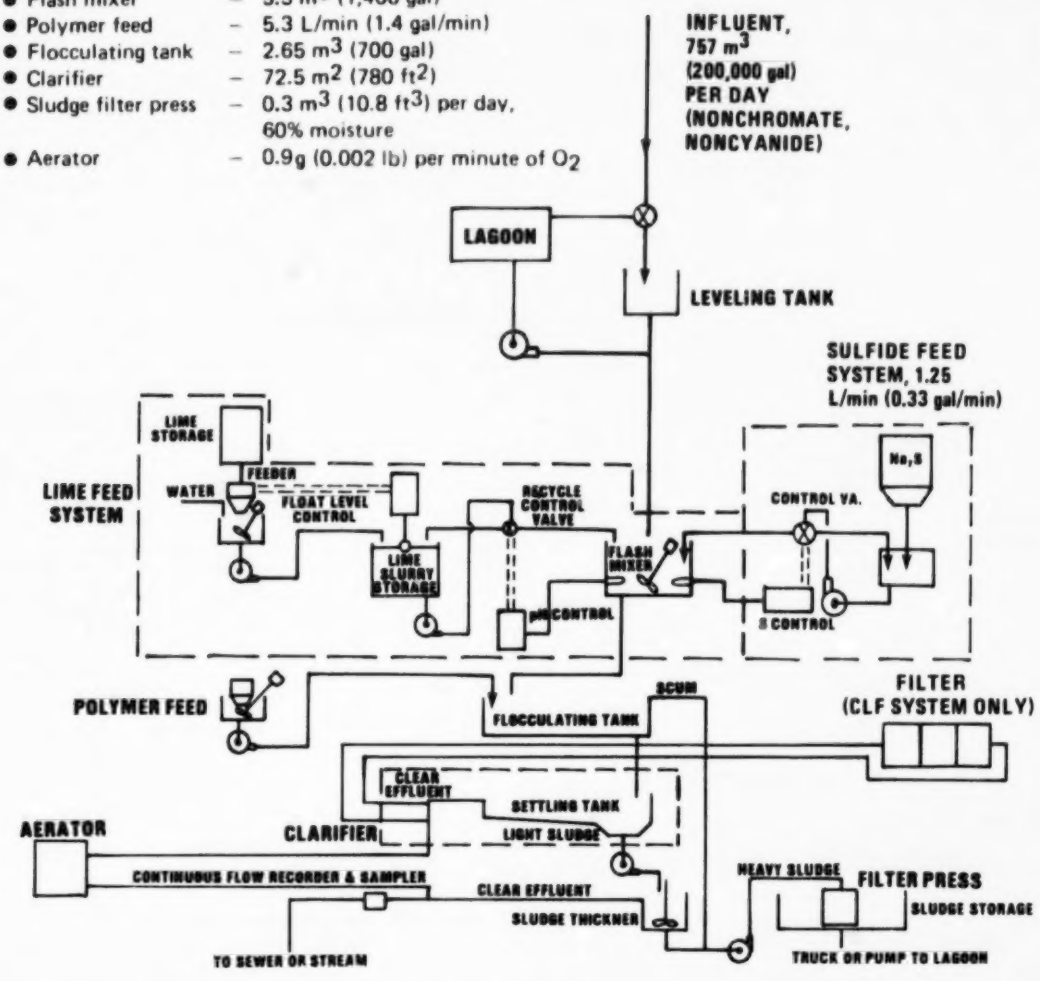


Figure F-5. Medium-sized LWS-CL and LWS-CLF plant schematic.

- Plant capacity = 1,893 m^3 (500,000 gal) per day

- Lagoon – 1,908 m^3 (504,000 gal)
- Leveling tank – 79.5 m^3 (21,000 gal)
- Lime feed – 2.5 L/min (0.66 gal/min)
- Flash mixer – 13.25 m^3 (3,500 gal)
- Polymer feed – 13.25 L/min (3.5 gal/min)
- Flocculating tank – 6.6 m^3 (1,750 gal)
- Clarifier – 182 m^2 (1,960 ft^2)
- Sludge filter press – 0.8 m^3 (27 ft^3) per day, 60% moisture

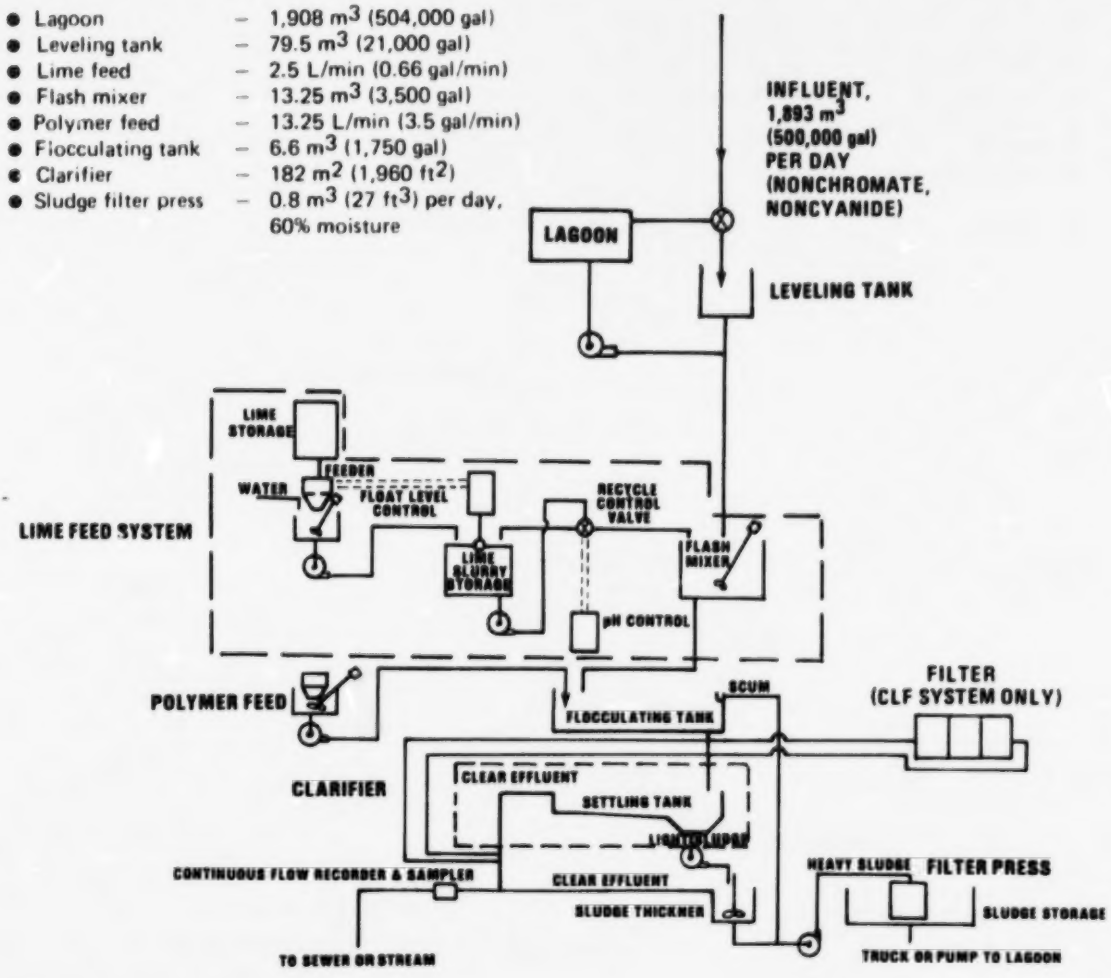


Figure F-6. Large LO-CL and LO-CLF plant schematic.

- Plant capacity = 1,893 m^3 (500,000 gal) per day

- Lagoon – 1,908 m^3 (504,000 gal)
- Leveling tank – 79.5 m^3 (21,000 gal)
- Lime feed – 2.5 L/min (0.66 gal/min)
- Flash mixer – 13.25 m^3 (3,500 gal)
- Polymer feed – 13.25 L/min (3.5 gal/min)
- Flocculating tank – 6.6 m^3 (1,750 gal)
- Clarifier – 182 m^2 (1,960 ft^2)
- Sludge filter press – 0.8 m^3 (27 ft^3) per day, 60% moisture
- Aerator – 2.7g (0.006 lb) per minute of O_2

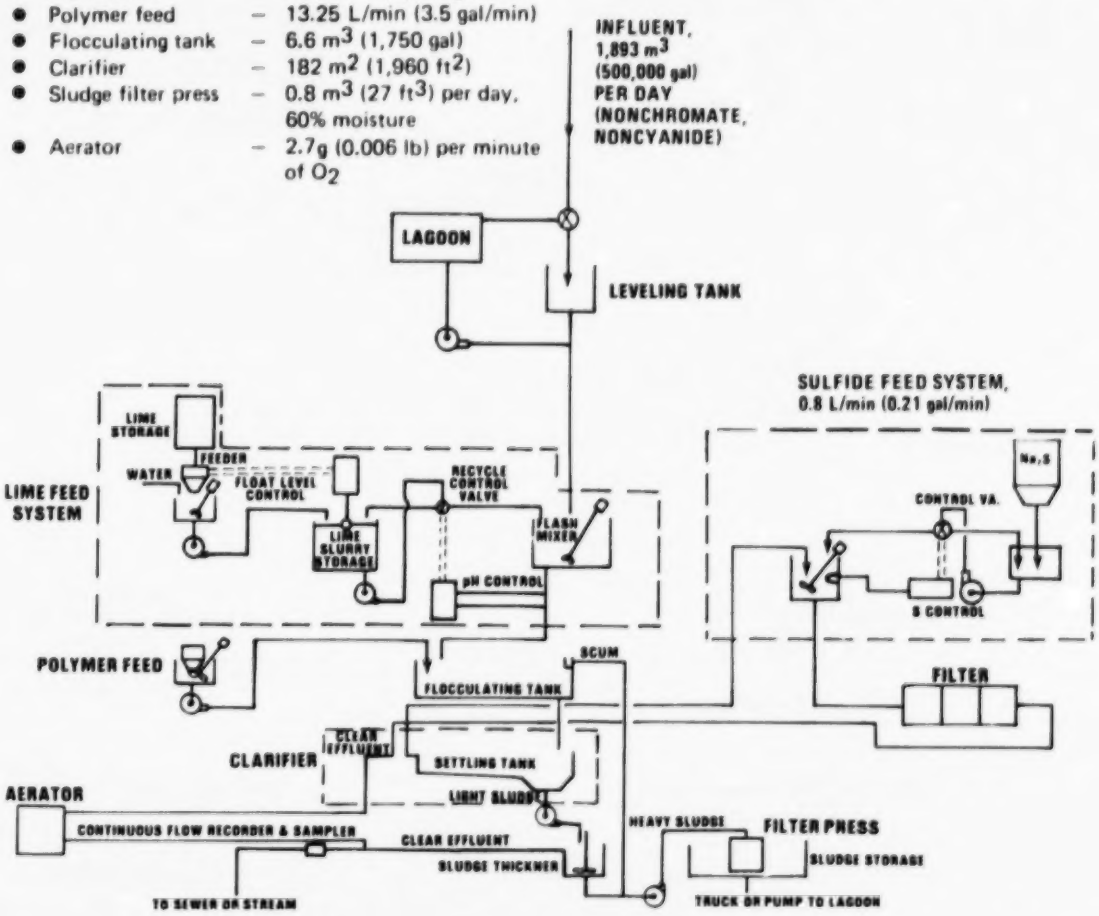


Figure F-7. Large LSPF plant schematic.

- Plant capacity = 1,893 m^3 (500,000 gal) per day

- Lagoon – 1,908 m^3 (504,000 gal)
- Leveling tank – 79.5 m^3 (21,000 gal)
- Lime feed – 2.5 L/min (0.66 gal/min)
- Flash mixer – 13.25 m^3 (3,500 gal)
- Polymer feed – 13.25 L/min (3.5 gal/min)
- Flocculating tank – 6.6 m^3 (1,750 gal)
- Clarifier – 182 m^2 (1,960 ft^2)
- Sludge filter press – 0.8 m^3 (27 ft^3) per day, 60% moisture
- Aerator – 2.7g (0.006 lb) per minute of O_2

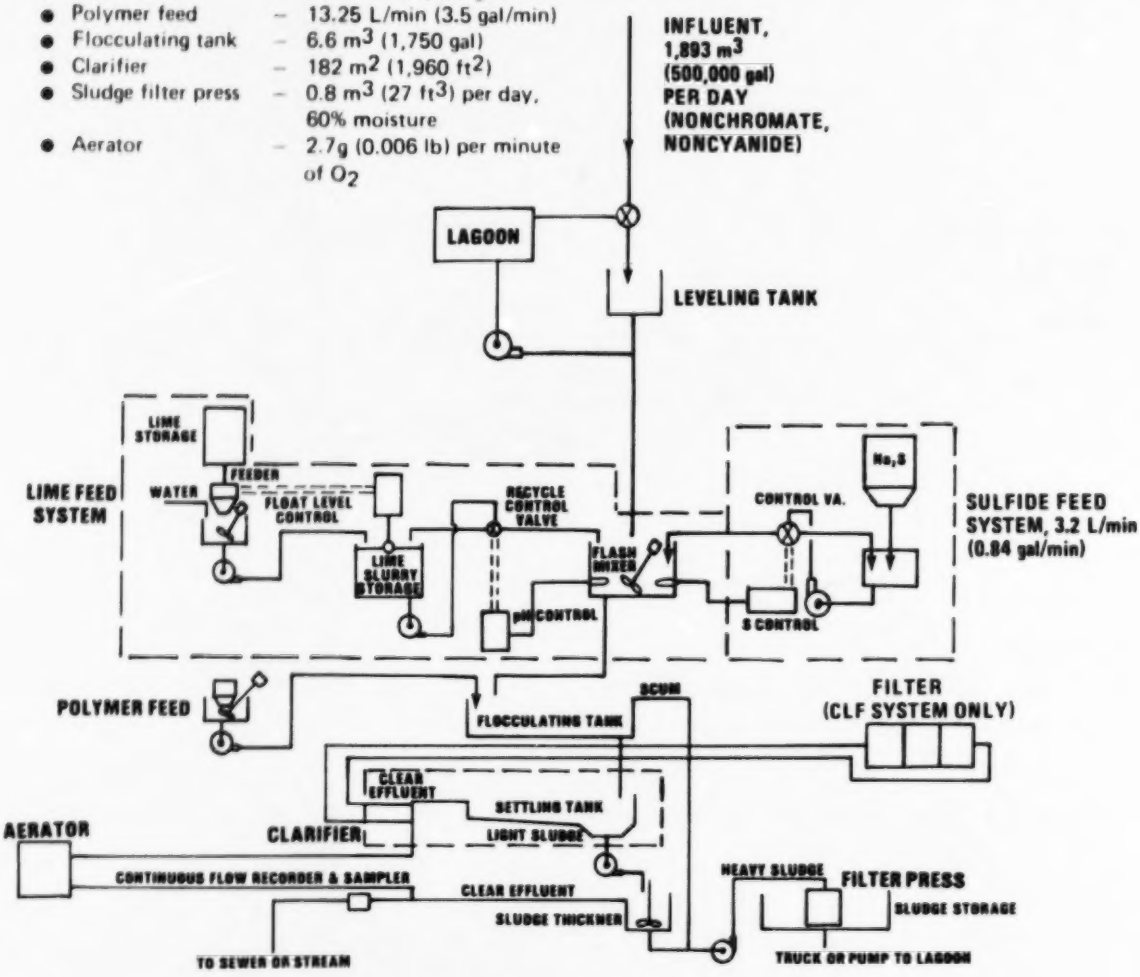


Figure F-8. Large LWS-CL and LWS-CLF plant schematic.

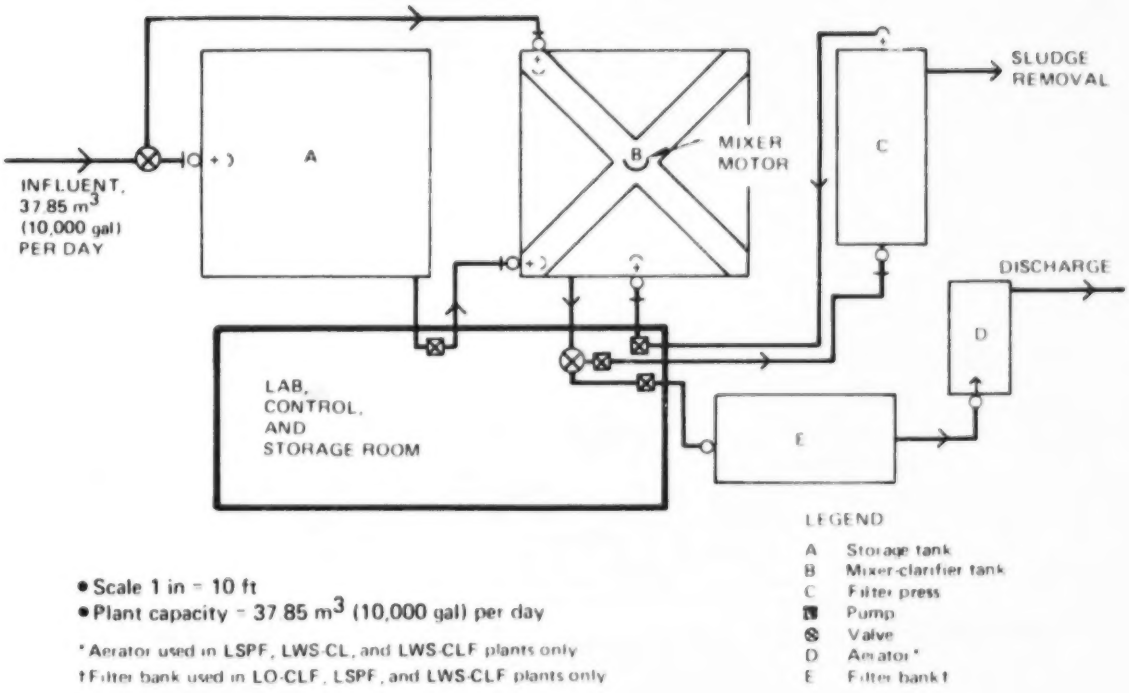
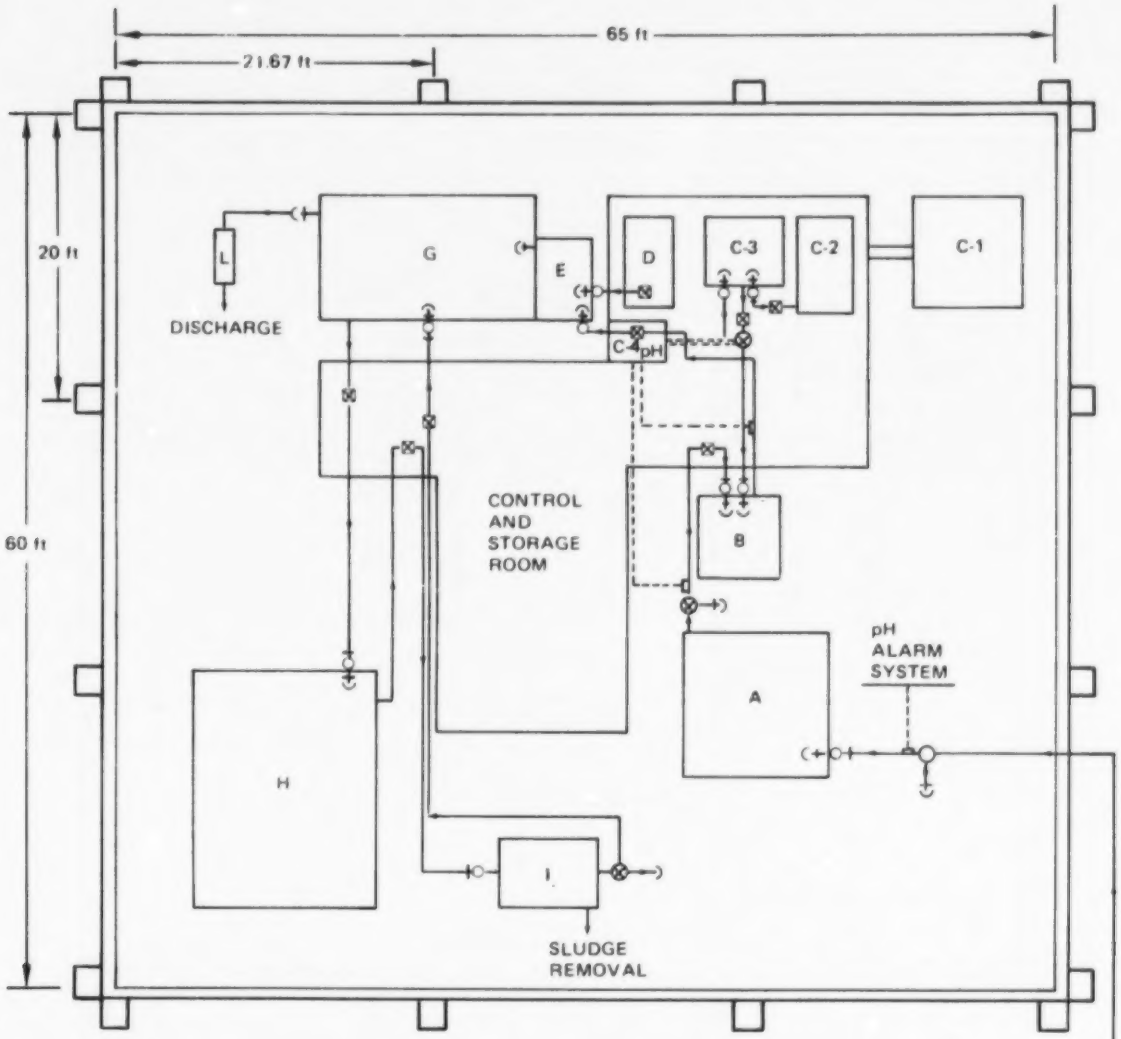


Figure F-9. Small plant layout--all processes (LO-CL, LO-CLF, LSPF, LWS-CL, and LWS-CLF).

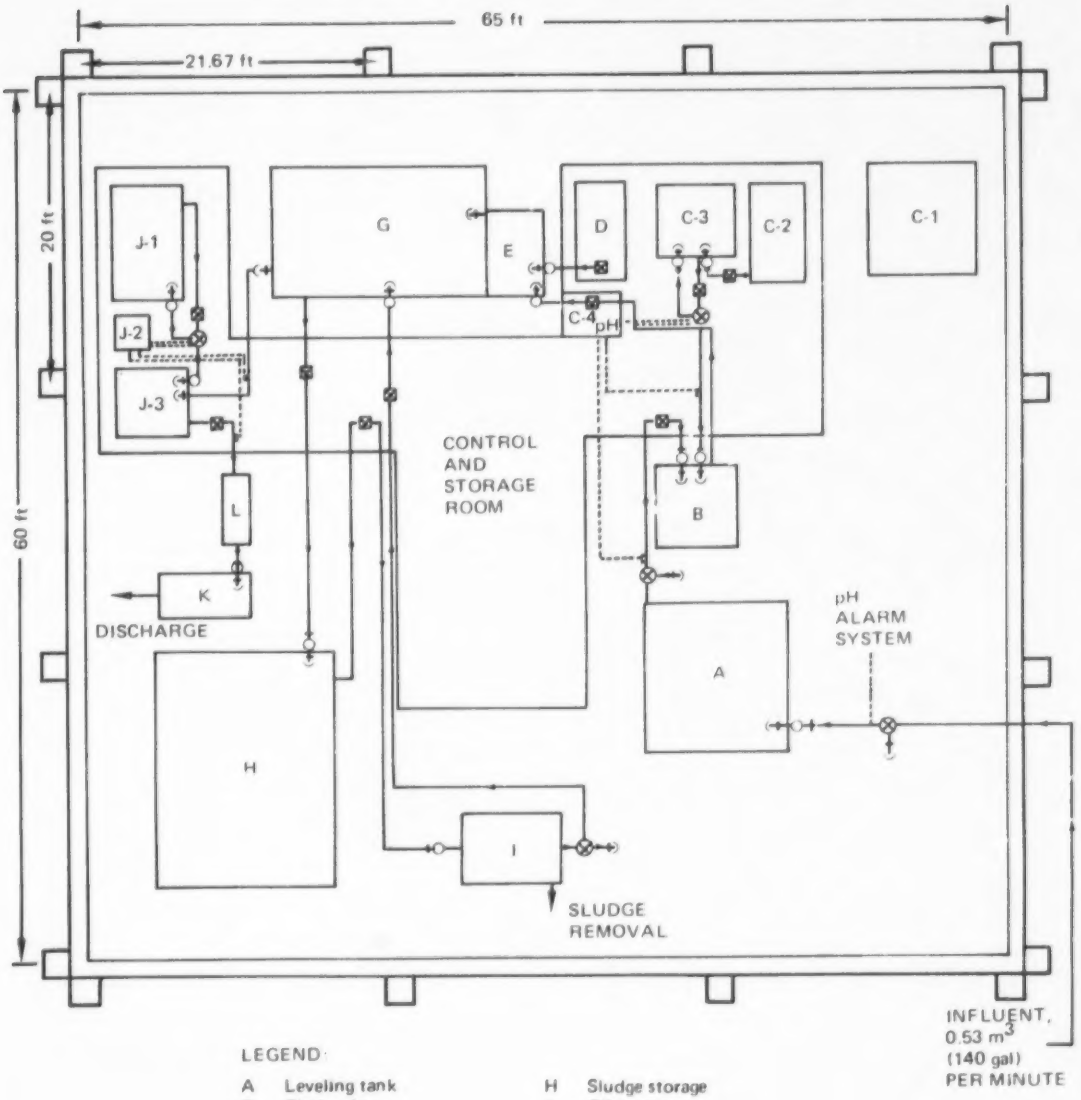


LEGEND:

A	Leveling tank	E	Flocculating tank
B	Flash mixer	G	Clarifier
C-1	Lime store	H	Sludge storage
C-2	Lime slaker	I	Filter press
C-3	Lime slurry	L	Filter (CLF system only)
C-4	pH control	⊠	Pump
D	Polymer feed	⊗	Valve

● Plant capacity = 757 m^3 (200,000 gal) per day

Figure F-10. Medium-sized LO-CL and LO-CLF plant layout.



LEGEND

A	Leveling tank	H	Sludge storage
B	Flash mixer	I	Filter press
C-1	Lime store	⊠	Pump
C-2	Lime slaker	⊗	Valve
C-3	Lime slurry	J-1	Sulfide feed
C-4	pH control	J-2	Sulfide control
D	Polymer feed	J-3	Sulfide slurry
E	Flocculating tank	K	Aerator
G	Clarifier	L	Filter

- Plant capacity = 757 m^3 (200,000 gal) per day

Figure F-11. Medium-sized LSPF plant layout.

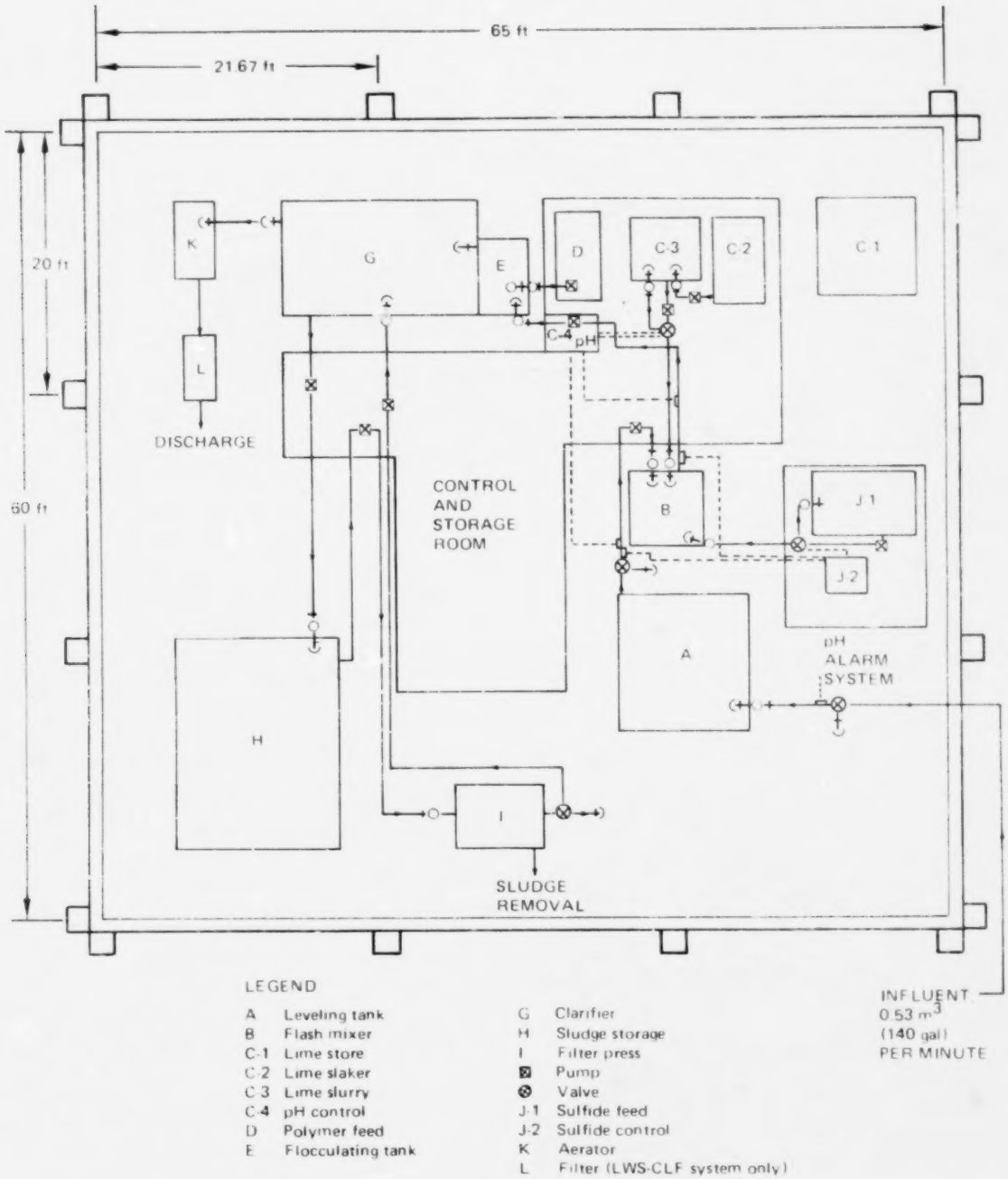
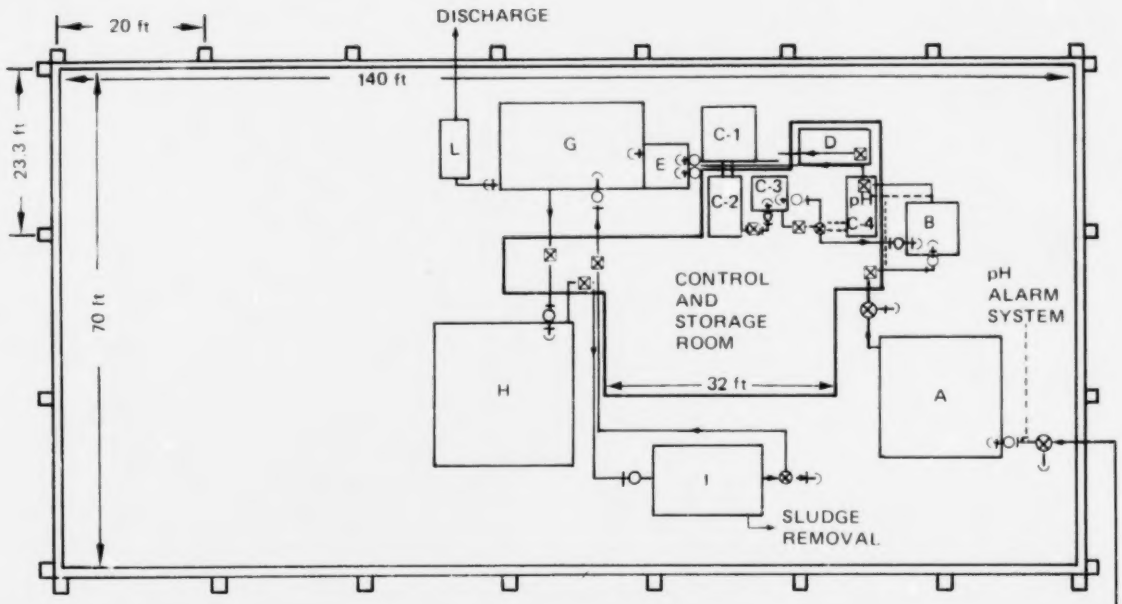


Figure F-12. Medium-sized LWS-CL and LWS-CLF plant layout.

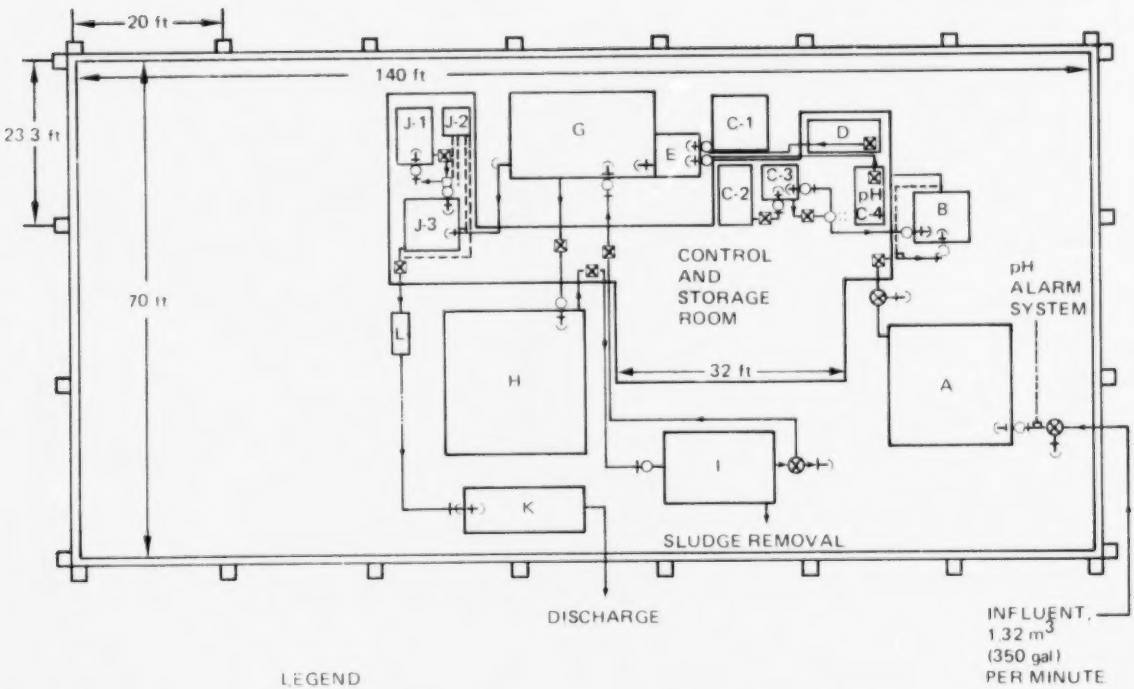


LEGEND:

A	Leveling tank	E	Flocculating tank
B	Flash mixer	G	Clarifier
C-1	Lime store	H	Sludge storage
C-2	Lime slaker	I	Filter press
C-3	Lime slurry	⊠	Pump
C-4	pH control	⊗	Valve
D	Polymer feed	L	Filter (LO-CLF system only)

- Plant capacity = 1,893 m^3 (500,000 gal) per day

Figure F-13. Large LO-CL and LO-CLF plant layout.

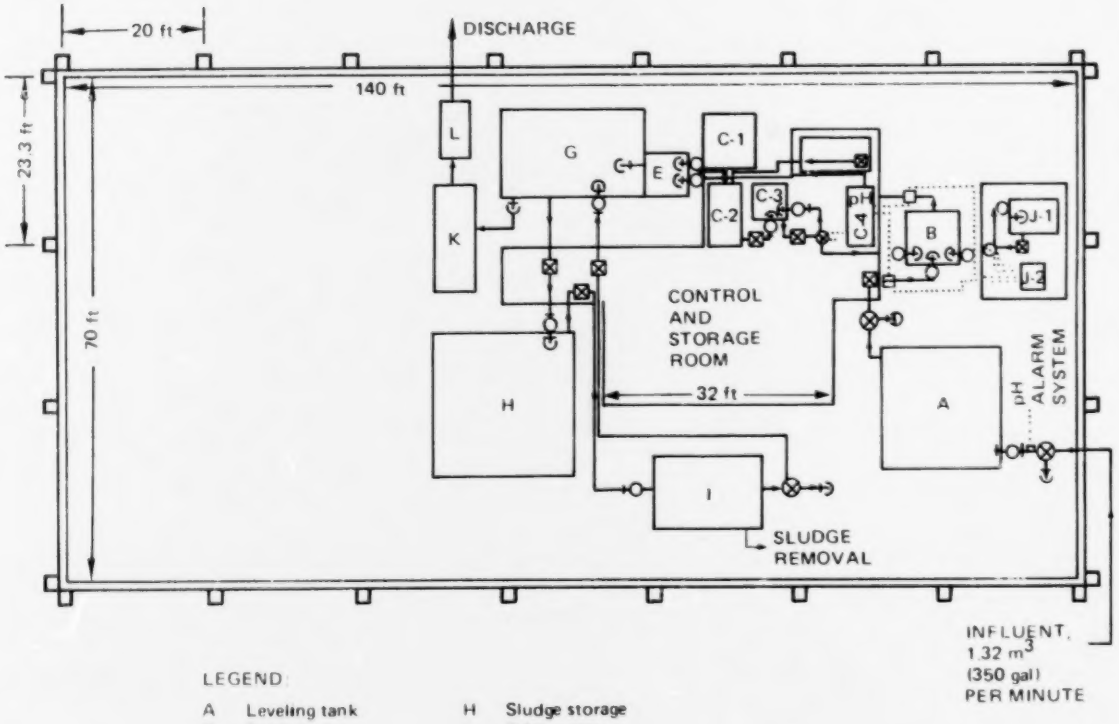


LEGEND

A	Leveling tank	H	Sludge storage
B	Flash mixer	I	Filter press
C-1	Lime store	⊠	Pump
C-2	Lime slaker	⊗	Valve
C-3	Lime slurry	J-1	Sulfide feed
C-4	pH control	J-2	Sulfide control
D	Polymer feed	J-3	Sulfide slurry
E	Flocculating tank	K	Aerator
G	Clarifier	L	Filter

- Plant capacity = 1,893 m^3 (500,000 gal) per day

Figure F-14. Large LSPF plant layout.



LEGEND

A	Leveling tank	H	Sludge storage
B	Flash mixer	I	Filter press
C-1	Lime store	⊠	Pump
C-2	Lime slaker	⊗	Valve
C-3	Lime slurry	J-1	Sulfide feed
C-4	pH control	J-2	Sulfide control
D	Polymer feed	K	Aerator
E	Flocculating tank	L	Filter (LWS-CLF system only)
G	Clarifier		

● Plant capacity = 1,893 m^3 (500,000 gal) per day

Figure F-15. Large LWS-CL and LWS-CLF plant layout.

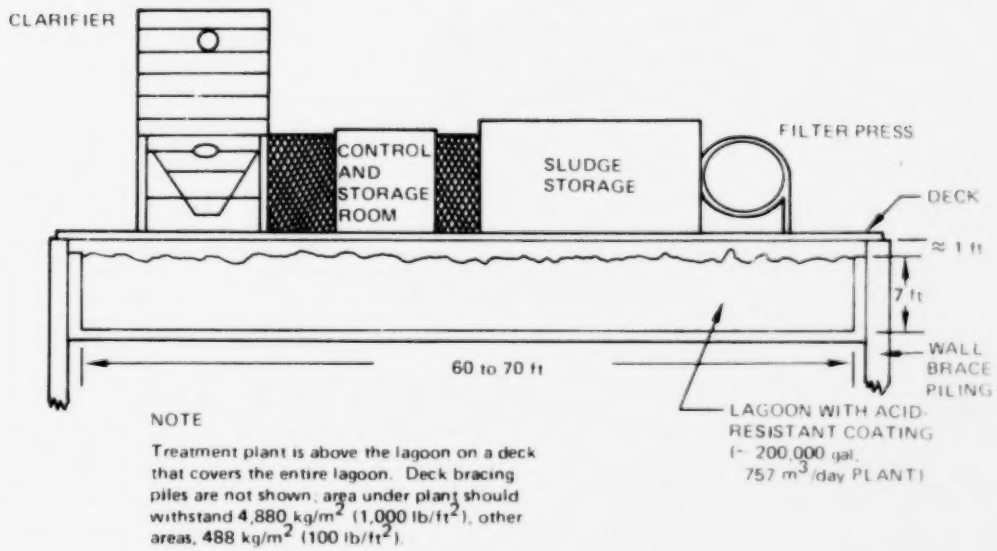

CLARIFIER
CONTROL AND STORAGE ROOM
SLUDGE STORAGE
FILTER PRESS
DECK
≈ 1 ft
7 ft
60 to 70 ft
WALL BRACE PILING
LAGOON WITH ACID-RESISTANT COATING
(~ 200,000 gal, 757 m3/day PLANT)
NOTE
Treatment plant is above the lagoon on a deck that covers the entire lagoon. Deck bracing piles are not shown; area under plant should withstand 4,880 kg/m2 (1,000 lb/ft2), other areas, 488 kg/m2 (100 lb/ft2).

Figure F-16. Cross section of medium-sized and large plants–all processes (LO-CL, LO-CLF, LSPF, LWS-CL, and LWS-CLF).

APPENDIX G

GRAPHIC PRESENTATION OF RESULTS

Figures G-1 through G-5 graphicaily compare the raw feed and effluent concentrations of cadmium, copper, chromium, nickel, and zinc heavy metals for the five precipitation processes:

a. Lime only, clarified (LO-CL)
b. Lime only, clarified and filtered (LO-CLF)
c. Lime, sulfide polished and filtered (LSPF)
d. Lime with sulfide, clarified (LWS-CL)
e. Lime with sulfide, clarified and filtered (LWS-CLF)

Figure G-1 shows the relationship of LO-CL process effluent concentrations for the 16 test runs. Similar bar graphs in groups of five each (Figures G-2 through G-5) show the same type of data for the other four processes.

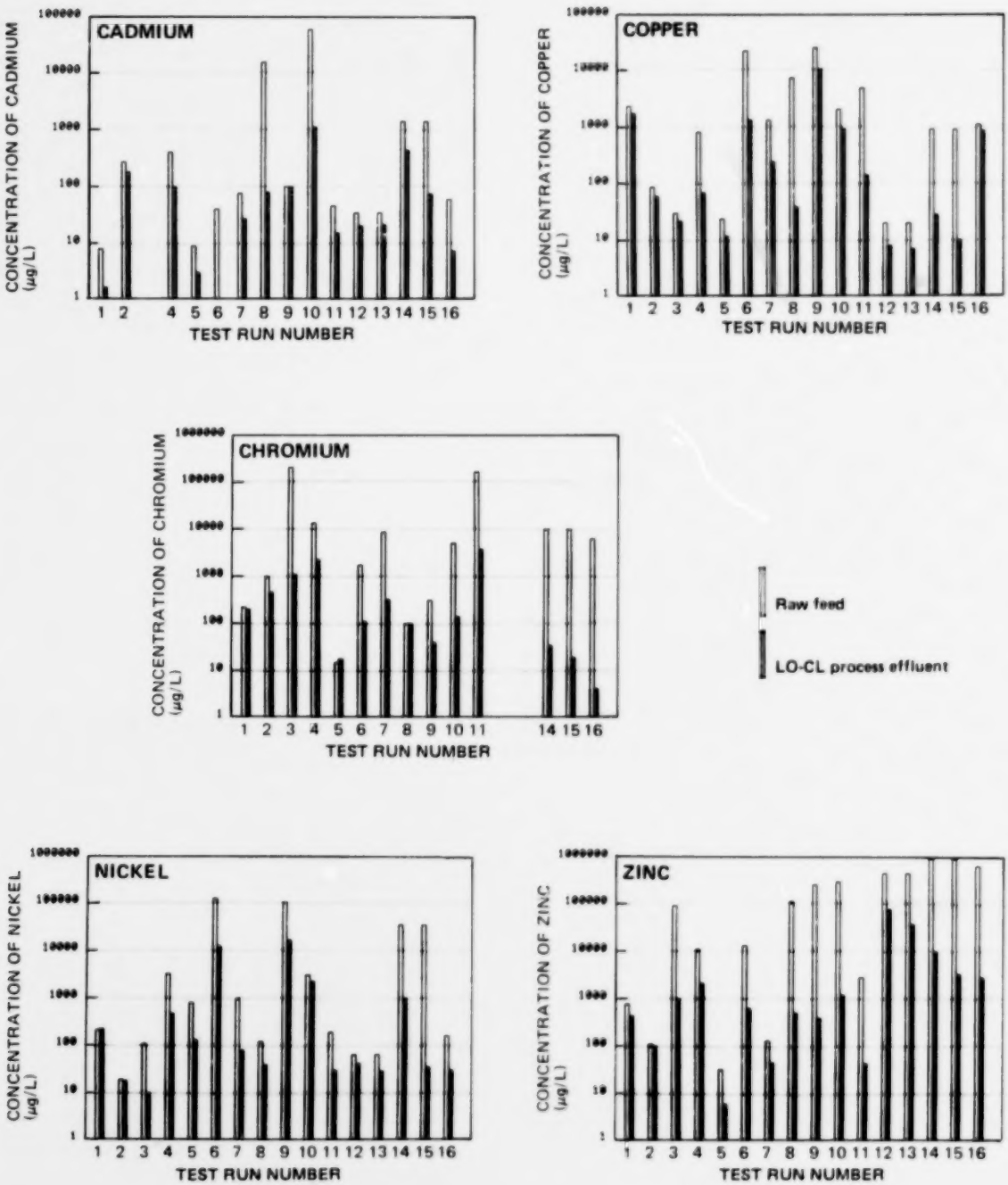


Figure G-1. Relationship of LO-CL process effluent concentration to raw feed concentration for Cd, Cu, Cr, Ni, and Zn.

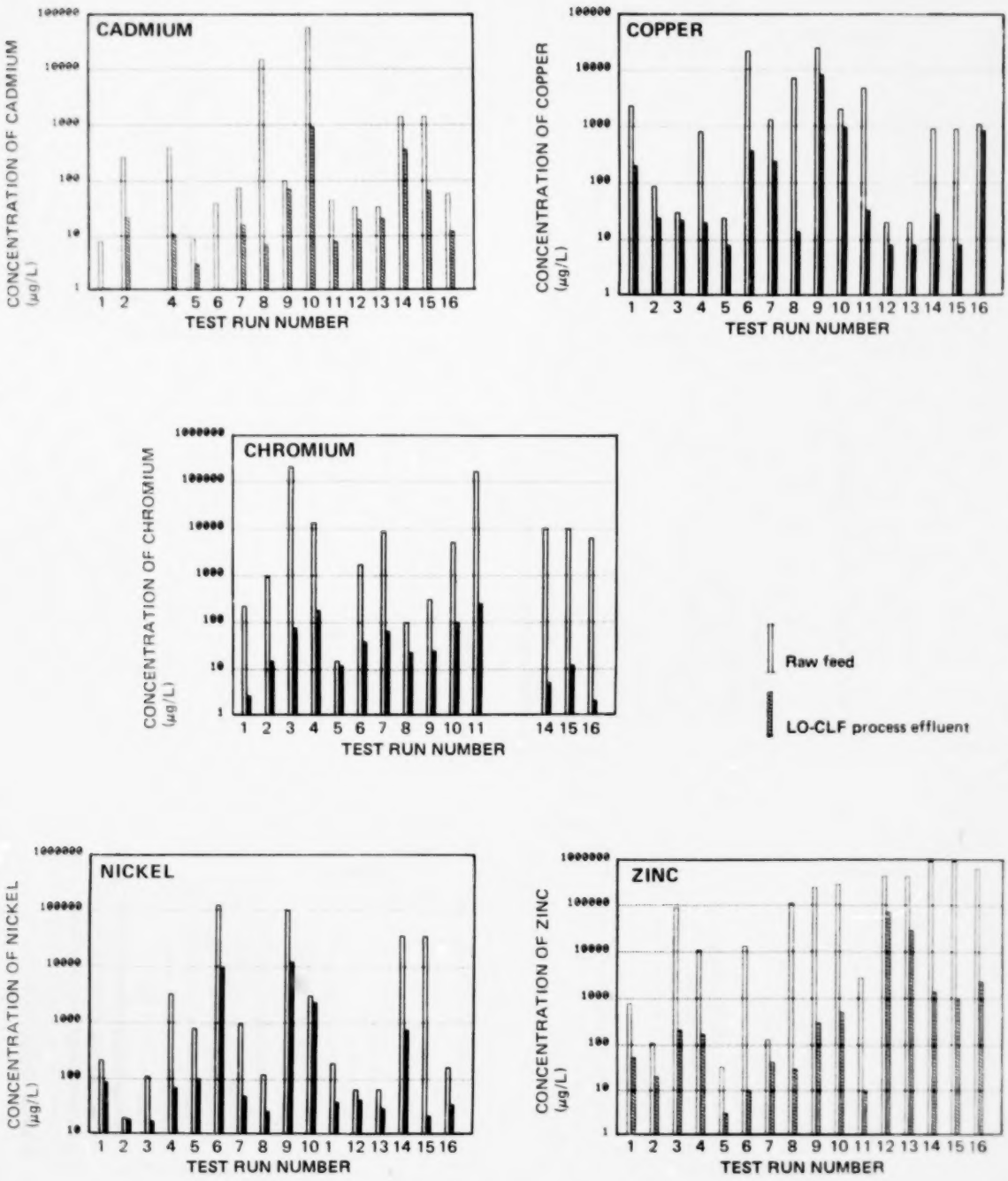


Figure G-2. Relationship of LO-CLF process effluent concentration to raw feed concentration for Cd, Cu, Cr, Ni, and Zn.

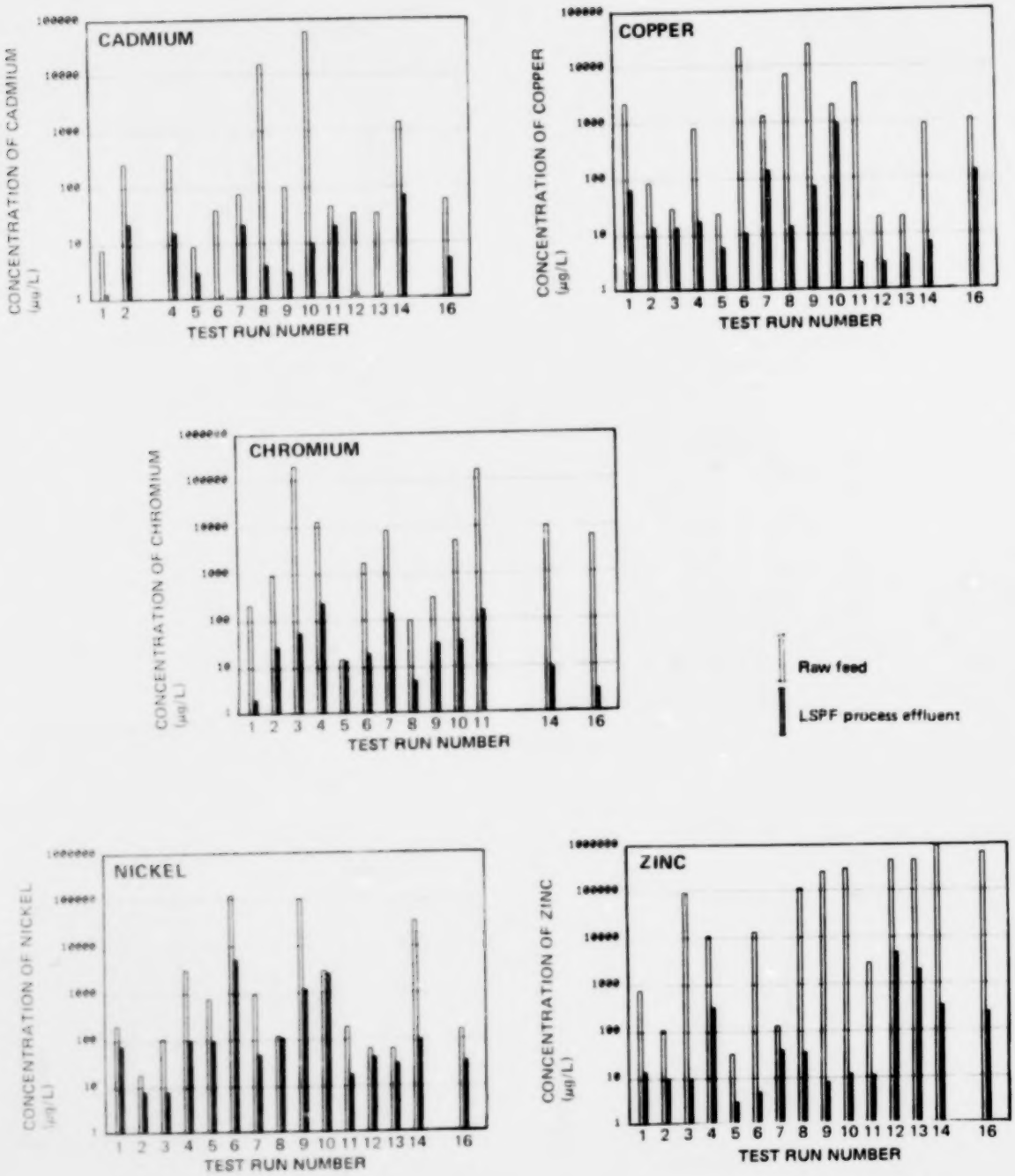


Figure G-3. Relationship of LSPF process effluent concentration to raw feed concentration for Cd, Cu, Cr, Ni, and Zn.

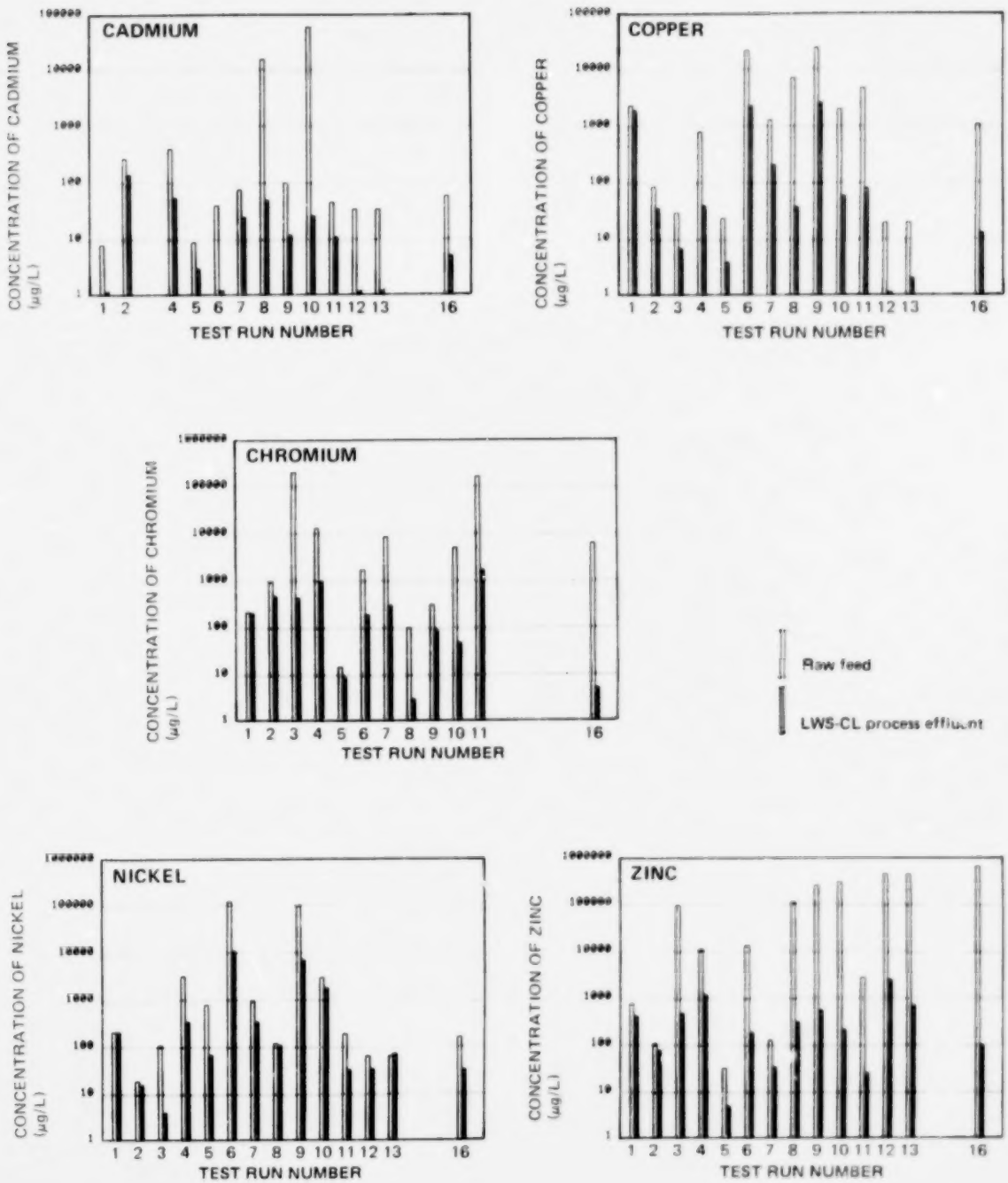


Figure G-4. Relationship of LWS-CL process effluent concentration to raw feed concentration for Cd, Cu, Cr, Ni, and Zn.

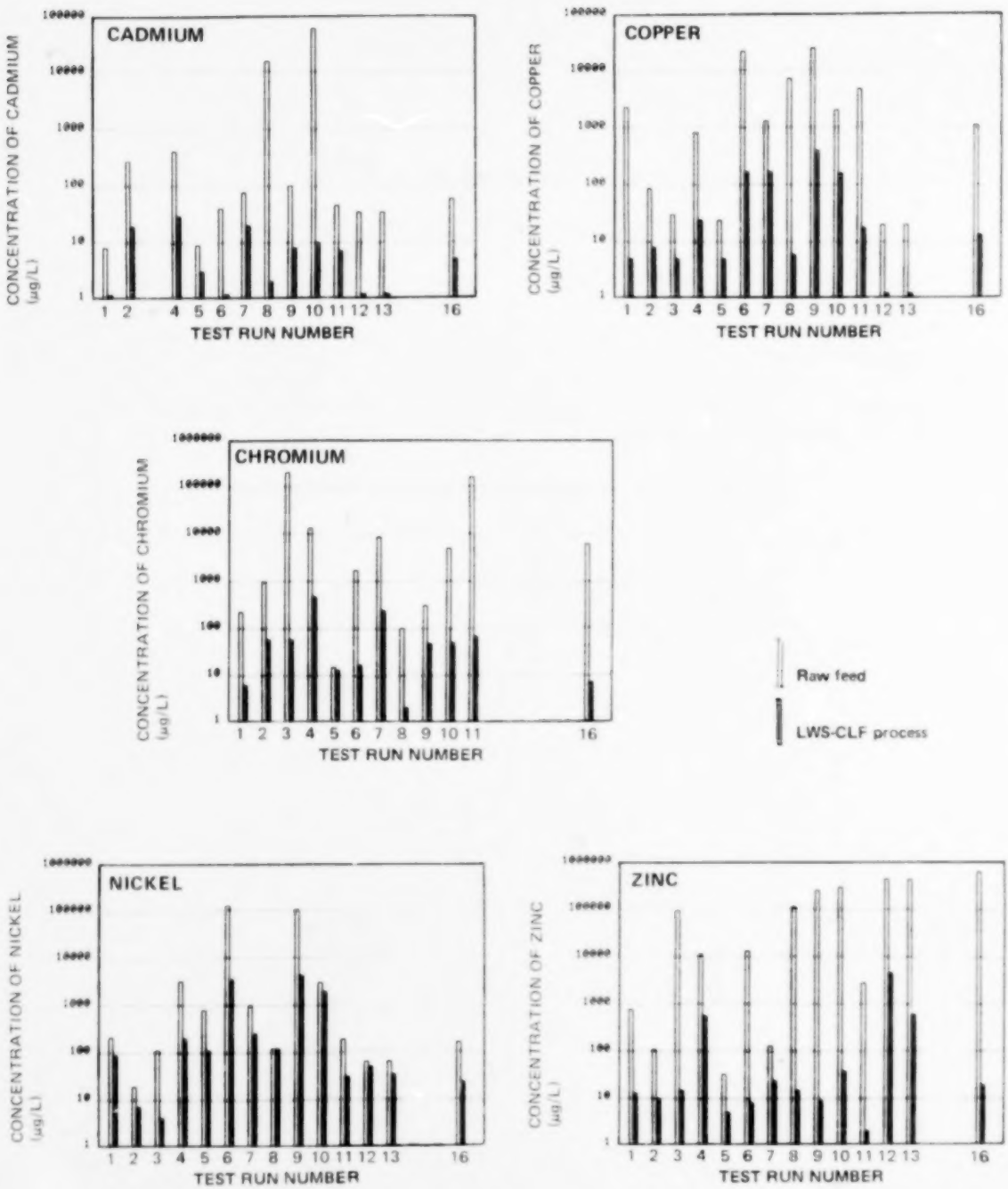


Figure G-5. Relationship of LWS-CLF process effluent concentration to raw feed concentration for Cd, Cu, Cr, Ni, and Zn.

APPENDIX H

CRITERIA FOR SELECTING pH VALUE FOR PRECIPITATION

Figure H-1, which indicates theoretical hydroxide solubilities (14), shows that the optimum pH for maximum precipitation varies for different metals. Consequently, a treatment plant that receives a mixed heavy metal load must adopt a compromise pH. The value will depend on the desired reduction levels for specific heavy metals. Two other factors are also usually taken into account. First, an unnecessarily high pH results in unnecessarily high lime costs. Second, subsequent acidification may be required, if the local discharge permit requires a maximum pH of 9.0, as many permits do.

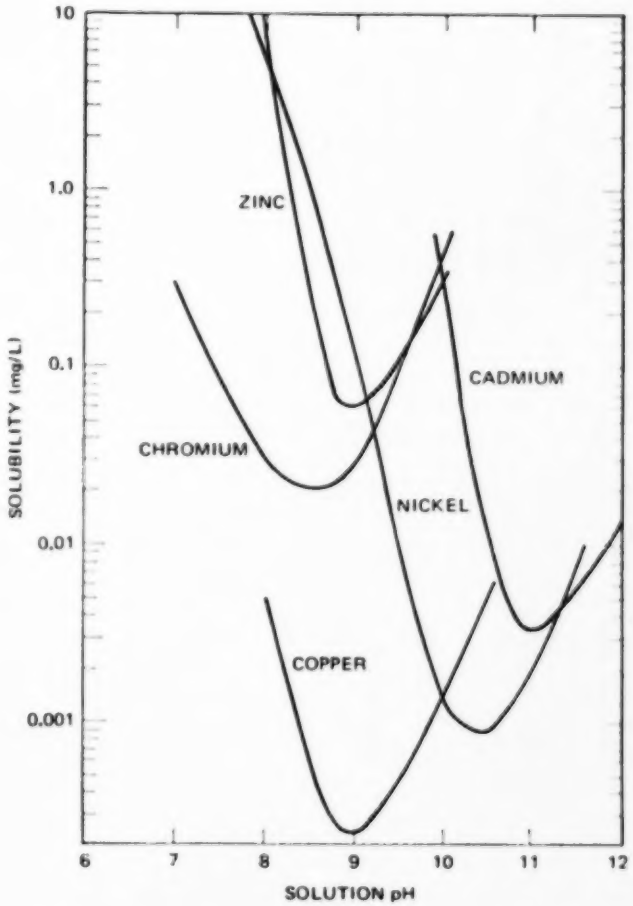


Figure H-1. Effect of pH on effluent concentration of heavy metals.

SELECTION OF pH VALUE

For this work, the preferred pH value was one that would reduce the heavy metal theoretical solubility levels below the EPA "1978 Proposed Effluent Limitation Guidelines" (14). The limits are listed in Table H-1.

Combination of the solubilities of Figure H-1 with the EPA guidelines generates Table H-2. Bold numbers in the table are levels below guideline limits.

TABLE H-1. PROPOSED EPA GUIDELINE LEVELS

Heavy metal	Proposed 30-day average efficient level (μg/L)
Cr^{6+}	90
Ag	340
Pb	400
Cd	500
Zn	1,500
Cr (total)	1,600
Ni	1,800
Cu	2,000

TABLE H-2. EFFLUENT CONCENTRATION RELATED TO EPA PROPOSED LIMITATIONS

Heavy metal	Concentration (μg/L)* at pH values of:										
	8.00	8.25	8.50	8.75	9.00	9.25	9.50	9.75	10.00	10.25	10.50
Cd	>1,300	>1,300	>1,300	>1,300	>1,300	>1,300	>1,300	1,300	**230**	**38**	**11**
Cr	**30**	**24**	**20**	**21**	**29**	**50**	**100**	**200**	**500**	**850**	2,000
Cu	**5**	**2**	**<1**	**<1**	**<1**	**<1**	**<1**	**<1**	**1.5**	**3**	**5**
Ni		2,800	**1,000**	**350**	**120**	**38**	**9**	**4**	**1.5**	**1**	**1**
Zn	8,000	**1,400**	**300**	**75**	**60**	**75**	**110**	**190**	**330**	**550**	**850**

*Boldface values are below EPA guideline levels.